Advantages of Multivariate Spectral Deconvolution Techniques in Correcting for Interferences in Beryllium Analysis by ICP-OES

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Office of Fossil Energy

Disclaimers

The findings and conclusions in this report are those of the author and do not necessarily represent the views of NETL-Albany.

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National Energy Technology Laboratory
Albany, Oregon

Focus: Materials process development and characterization.

Heavy historical emphasis in specialty metals research (e.g. zirconium, titanium, hafnium, niobium, metal alloying, metal separations).

History of NETL-Albany
http://www.netl.doe.gov/about/arc_history.html

Purpose of presentation

- Demonstrate that classical beryllium analysis by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) on real world samples is often biased due to the presence of poorly corrected spectral interference.

- Show that Multivariate Spectral Deconvolution can correct for these interference bias yielding accurate beryllium analysis results.

Critical references on Multivariate Spectral Deconvolution methods in ICP-OES analysis

David M. Haaland, William B. Chambers, Michael R. Keenan, and David K. Melgaard. Multi-window Classical Least Squares Multivariate Calibration Methods for Quantitative ICP-AES Analysis. Sandia National Laboratories. Albuquerque, NM. 1999

Oliveri et.al., 2006, Uncertainty estimation and figures of merit for multivariate calibration Pure Appl Chem. Vol. 78, No 3, pp. 633-661, (IUPAC technical report)

Nolte, Joachim, 2001. ICP Emission Spectroscopy. Wiley-VCH

Method definition

Generally known as multivariate calibration: usually the classical least squares (CLS) using a pseudo-inverse operation.

Represents the calibration derived from the total subarray beryllium spectra vector (II r* II) corrected for the interfering spectra vectors

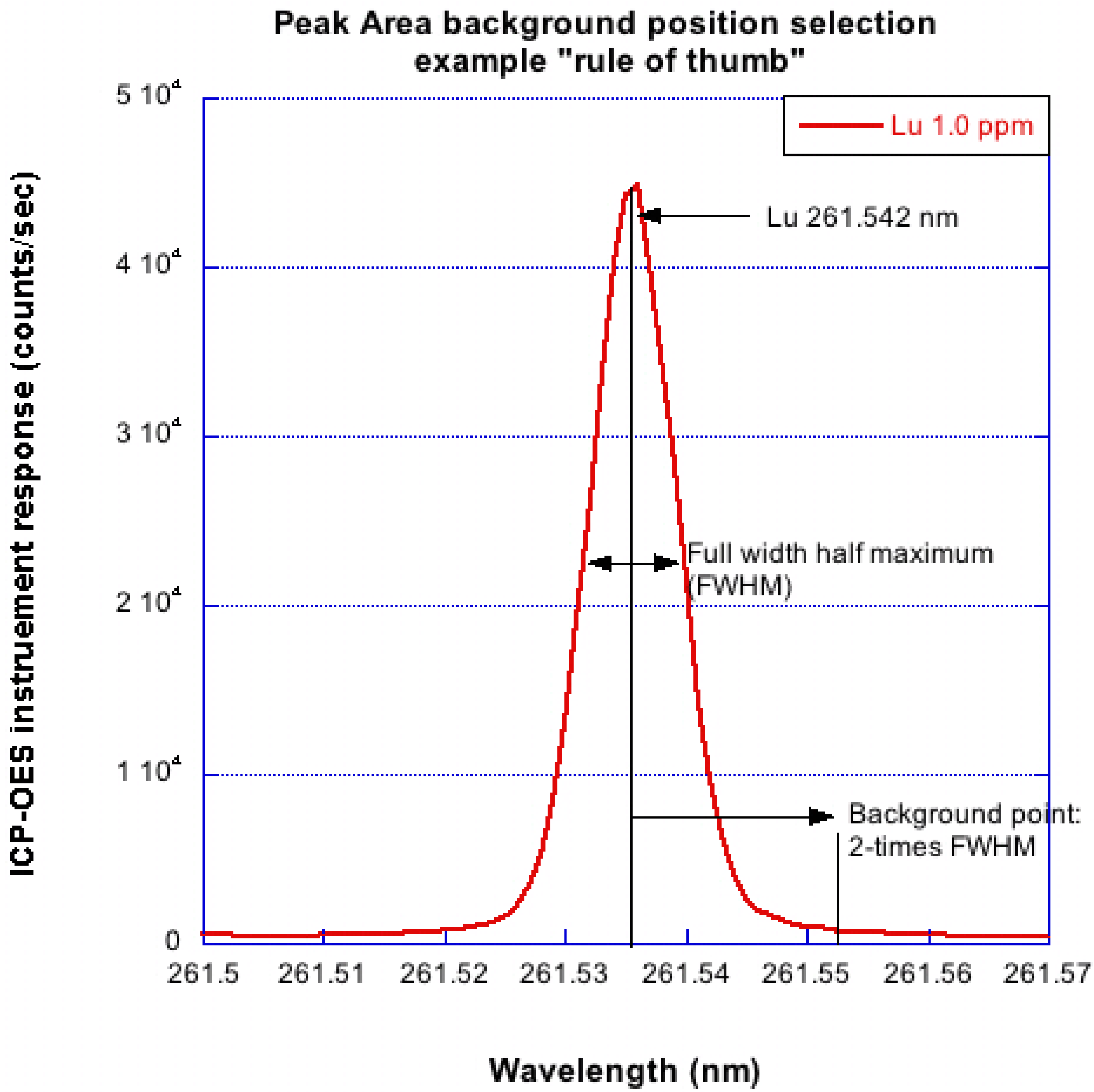
Implemented in ICP-OES analysis by PerkinElmer as Multi-component Spectral Fitting (MSF) and by Varian as the Fast Automatic Curve-Fitting Technique (FACT)

General peak measurement decision steps in ICP-OES analysis

Interference condition	Recommended solution
IF: Clean interference free analyte peak exists.	Use peak area/height with 1-2 point background correction.
IF: Interferent peak partially overlaps on analyte peak.	Use multivariate spectra deconvolution.
IF: interferent peak is a <u>direct</u> overlap on analyte peak.	Inter-element correction (IEC) OR: Chemical pre-separation or Alternative analysis method such as optical fluorescence.

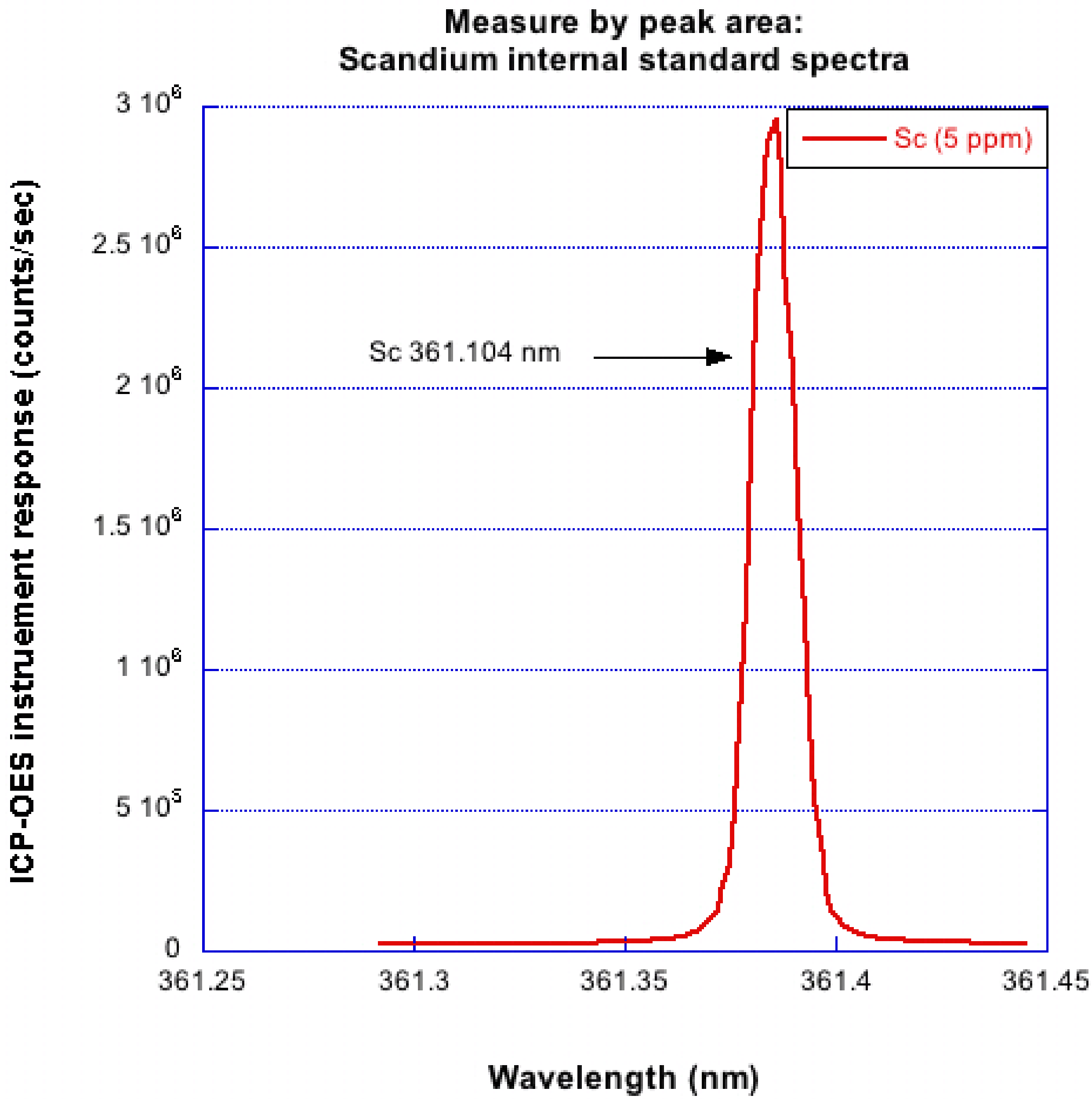
Requirements for selecting background correction points in classical ICP-OES.

- **Sloping baseline requires <u>two</u> background points.**
- **Flat baseline allows use of <u>one</u> background point. (two points reduces the signal/noise ratio).**
- **Background point(s) must be free of interferences.**
- **Background points must not be in wings of analyte line. (e.g. at twice the Full Width Half Height distance)**

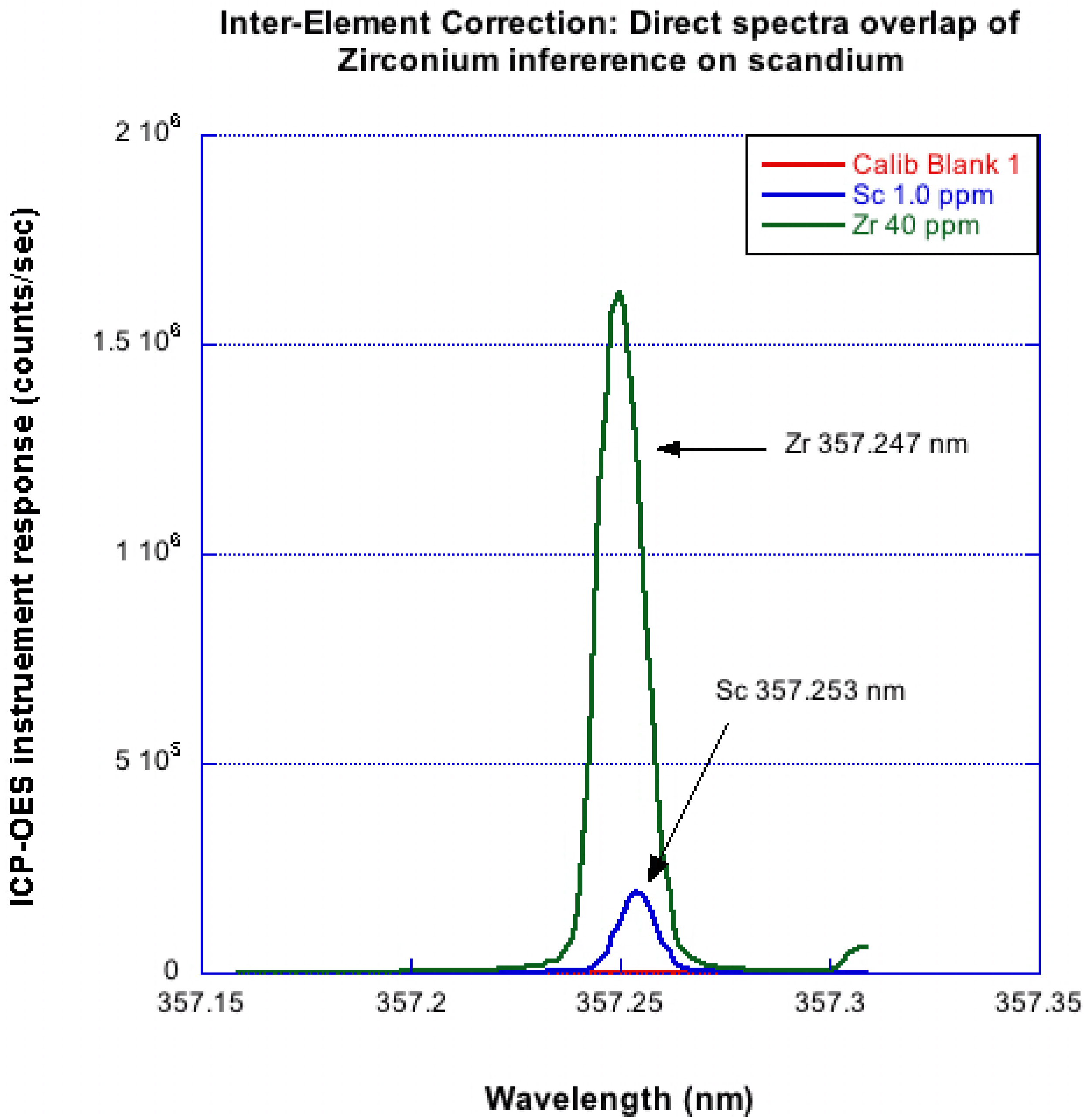


Peak Area background position selection
example "rule of thumb"
ICP-OES instruement response (counts/sec)
5 10⁴
4 10⁴
3 10⁴
2 10⁴
1 10⁴
0
Lu 1.0 ppm
Lu 261.542 nm
Full width half maximum
(FWHM)
Background point:
2-times FWHM
261.5
261.51
261.52
261.53
261.54
261.55
261.56
261.57
Wavelength (nm)

Peak area measurement example



IEC measurement example



Problems with peak area and IEC interference correction methods for beryllium analysis by ICP-OES

- **Multiple interferent spectra overlaps on the analyte peak(s).**

- **Absence of a <u>clean</u> background correction point for the 313.107, 313.042 and 234.065 nm beryllium lines in the presence of interferences.**

Potential spectral interferences bias in beryllium analysis at NETL-Albany

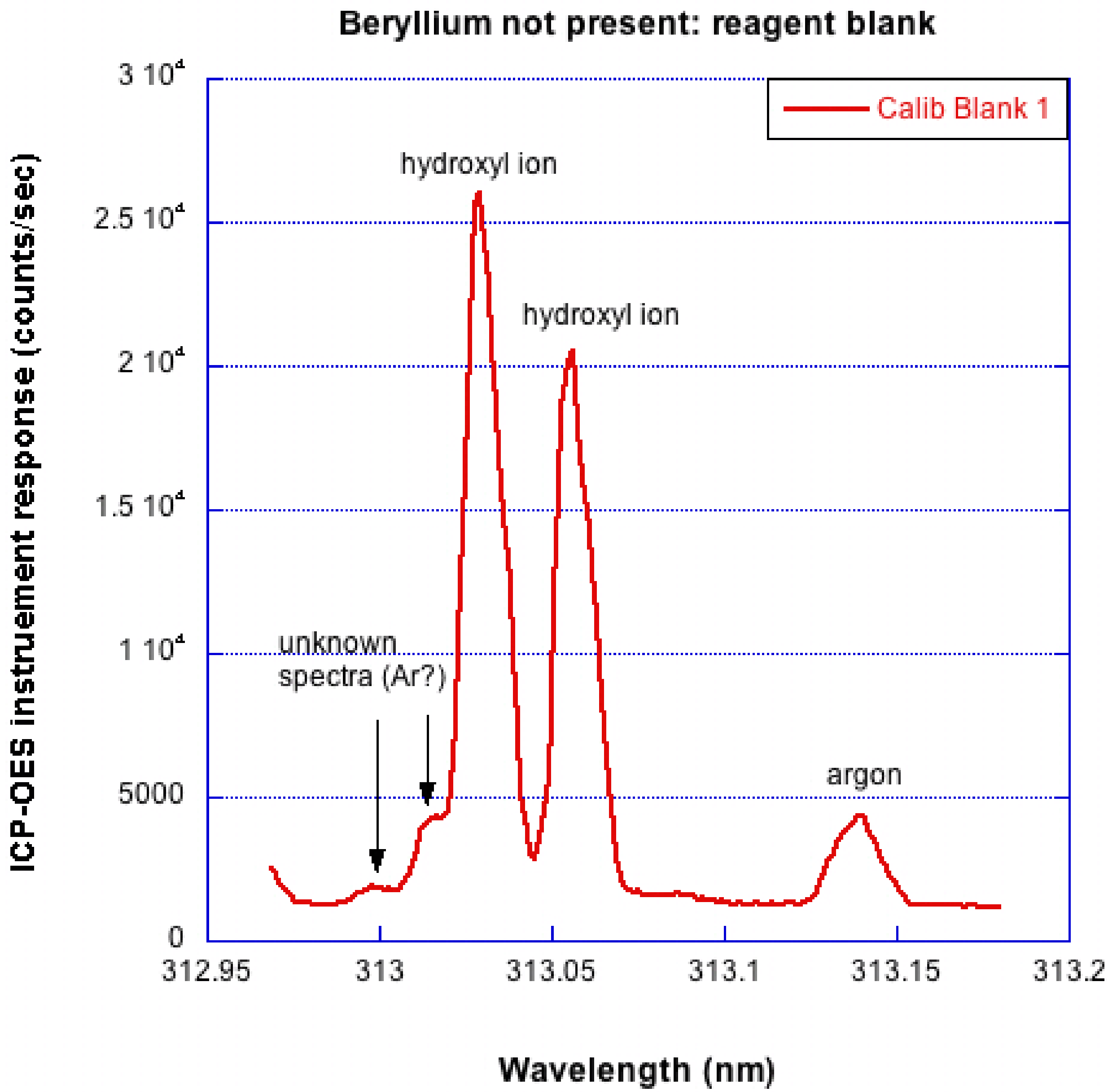
- **Common metal interferences**
  - Zirconium
  - Vanadium
  - Titanium
  - Chromium
- **Uncommon metal interferences**
  - Molybdenum
  - Niobium (Columbium)
  - Cerium (except in digests containing soluble HF)
  - Thulium

Only considered in radioactive work: Thorium, Uranium, and Plutonium.

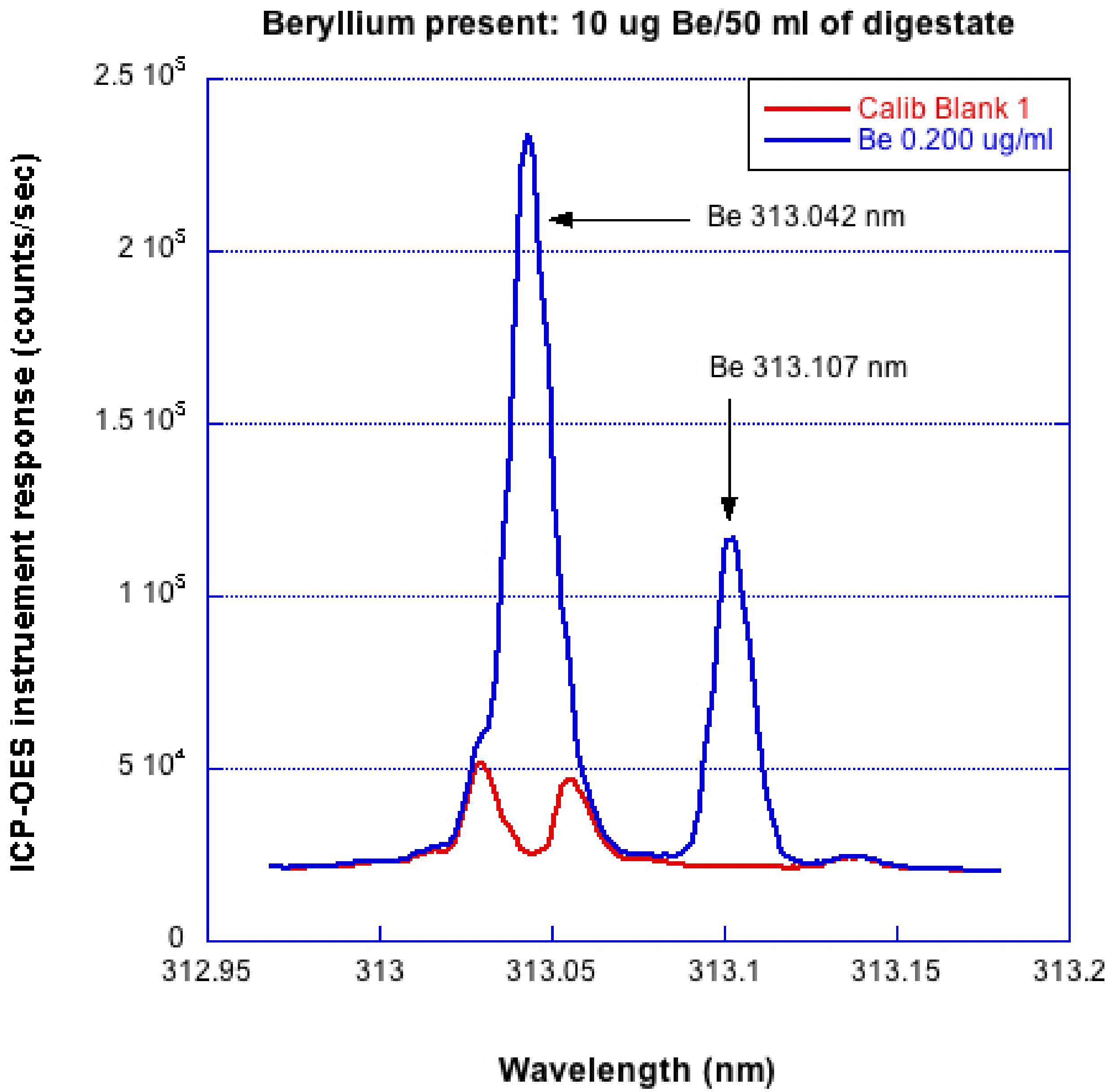
Samples with no significant measurement bias

	Beryllium is present	Beryllium is absent
Detected	**Correct decision**	**Incorrect Decision False Positive (Type I error)**
Not detected	**Incorrect decision False Negative (Type II error)**	**Correct decision**

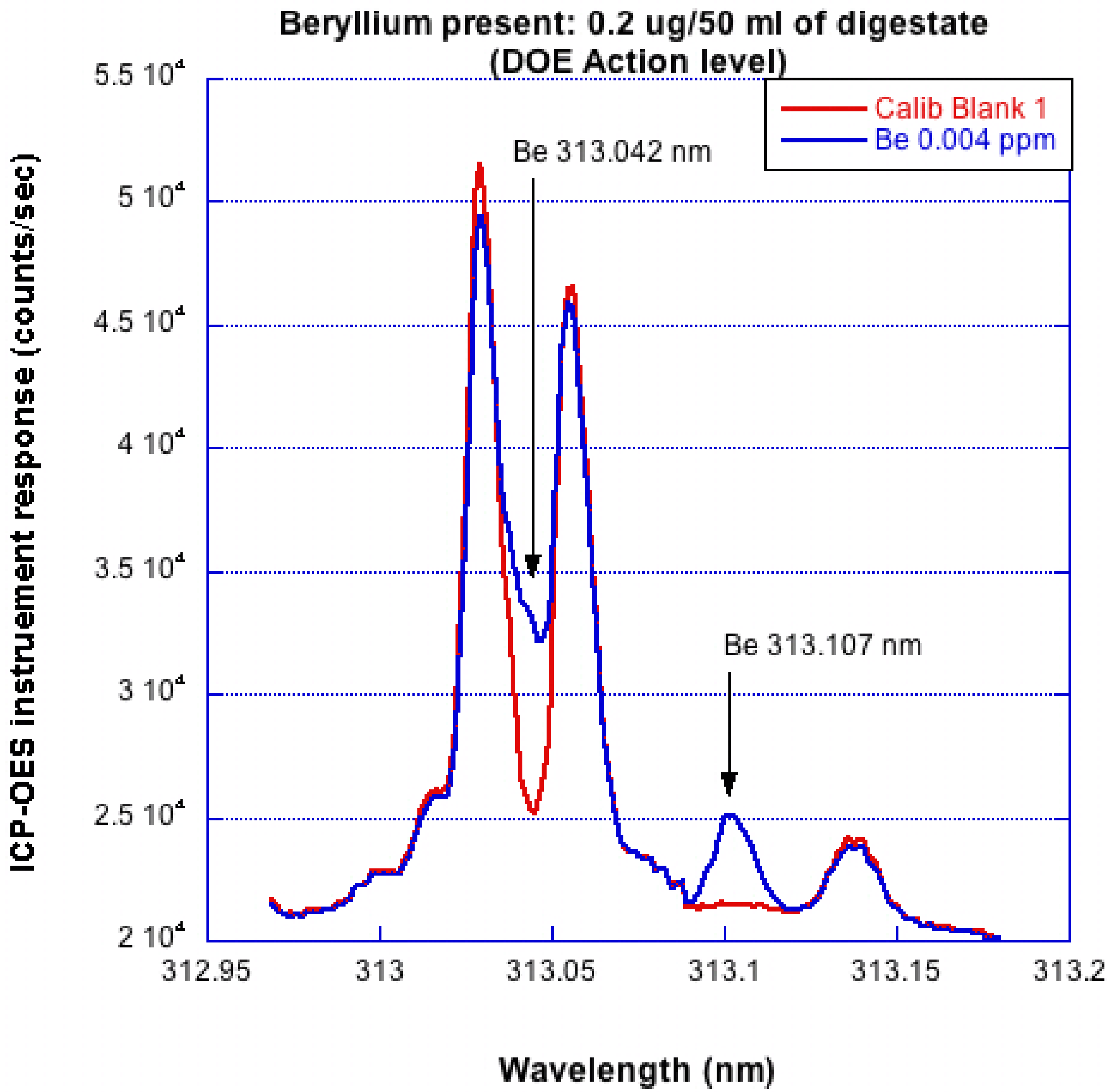
Blank showing structured plasma background lines



Pure beryllium no interferences



Pure beryllium at DOE action level: no interferences

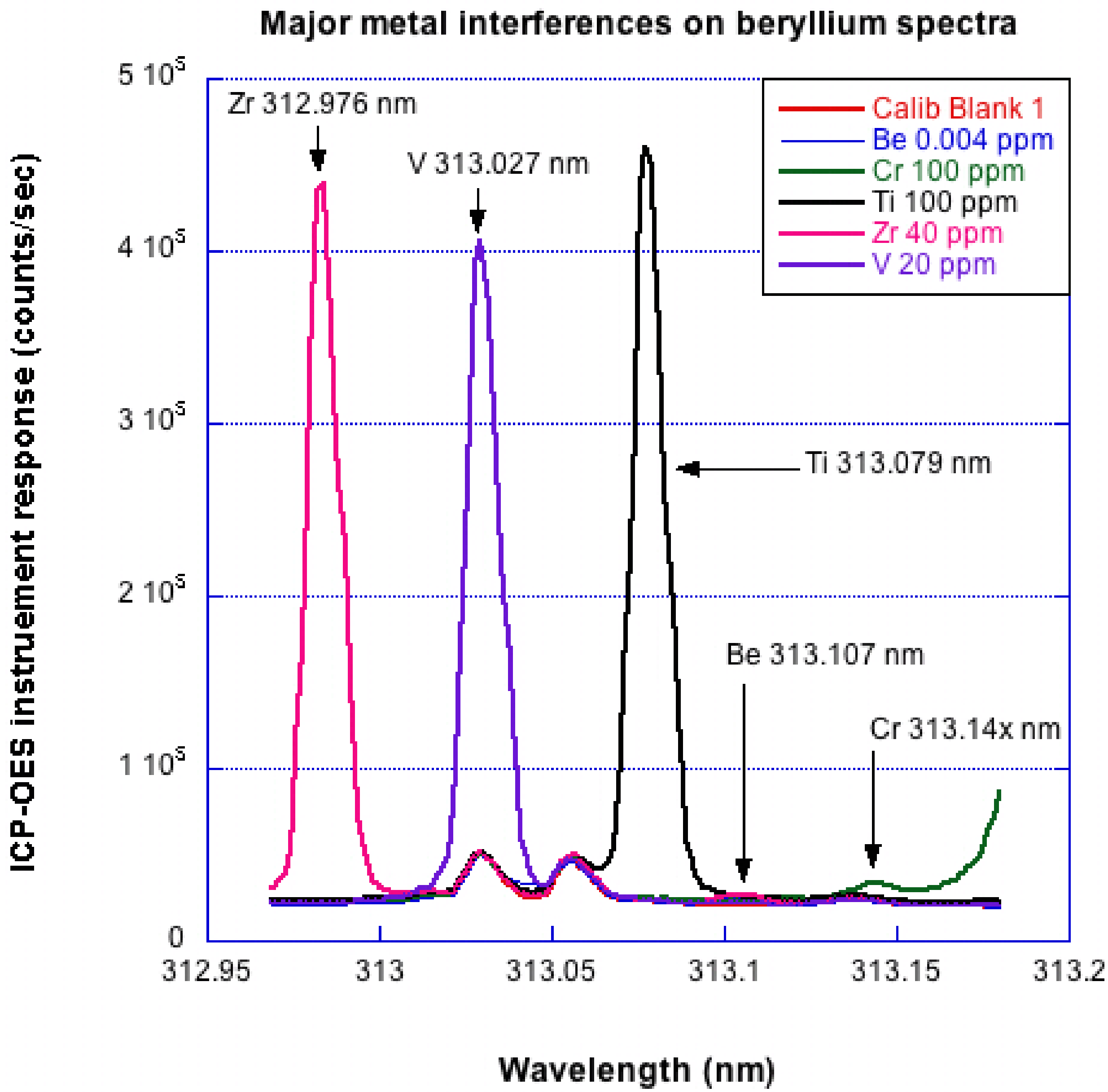


Samples with positive measurement bias due to interferences

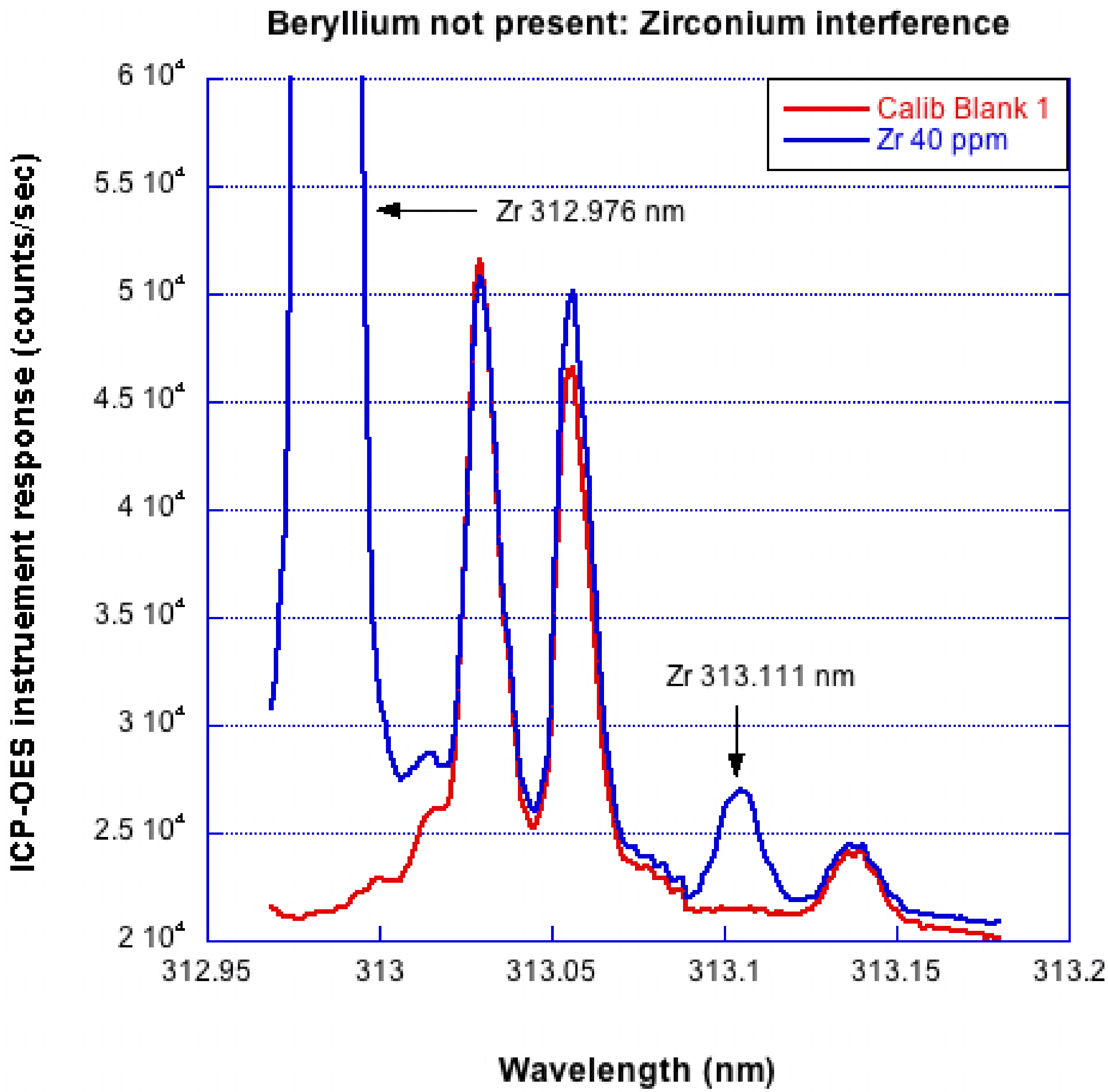
	Beryllium is present	Beryllium is absent
Detected	**Correct decision**	**Incorrect Decision False Positive (Type I error)**
Not detected	**Incorrect decision False Negative (Type II error)**	**Correct decision**

Major metal spectral interferences on beryllium 313.042 nm and 313.107 nm lines

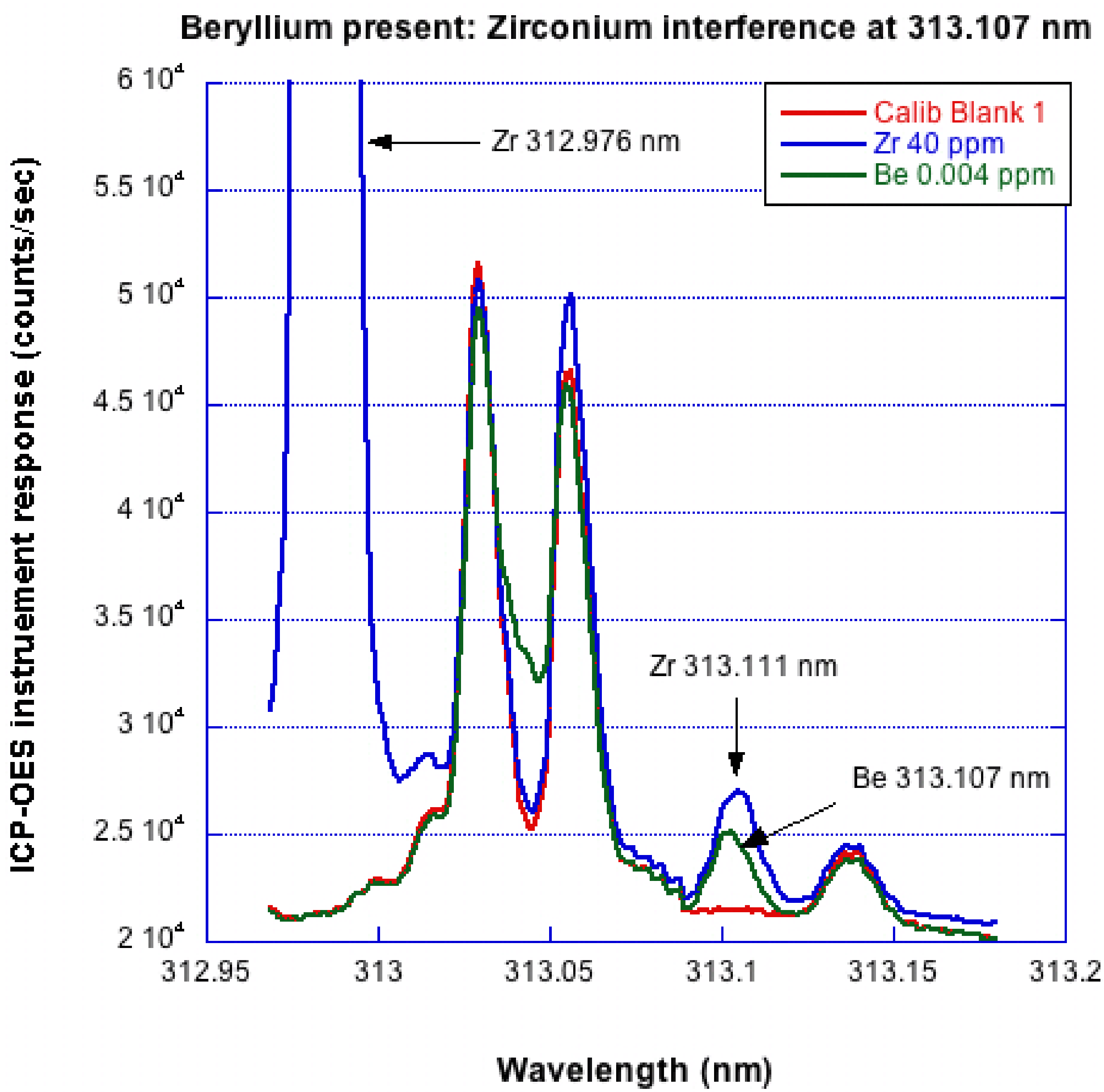
Element	state	Wavelength (nm)
Zirconium	I II	313.111 312.976
Vanadium	II	313.027
Titanium	II	313.079 313.175 (approximate)
Chromium	II	313.121 313.14x (approximate) 313.206


Major metal interferences on beryllium spectra
Zr 312.976 nm
V 313.027 nm
Ti 313.079 nm
Be 313.107 nm
Cr 313.14x nm
Calib Blank 1
Be 0.004 ppm
Cr 100 ppm
Ti 100 ppm
Zr 40 ppm
V 20 ppm
ICP-OES instruement response (counts/sec)
Wavelength (nm)
0
1 10^5
2 10^5
3 10^5
4 10^5
5 10^5
312.95
313
313.05
313.1
313.15
313.2

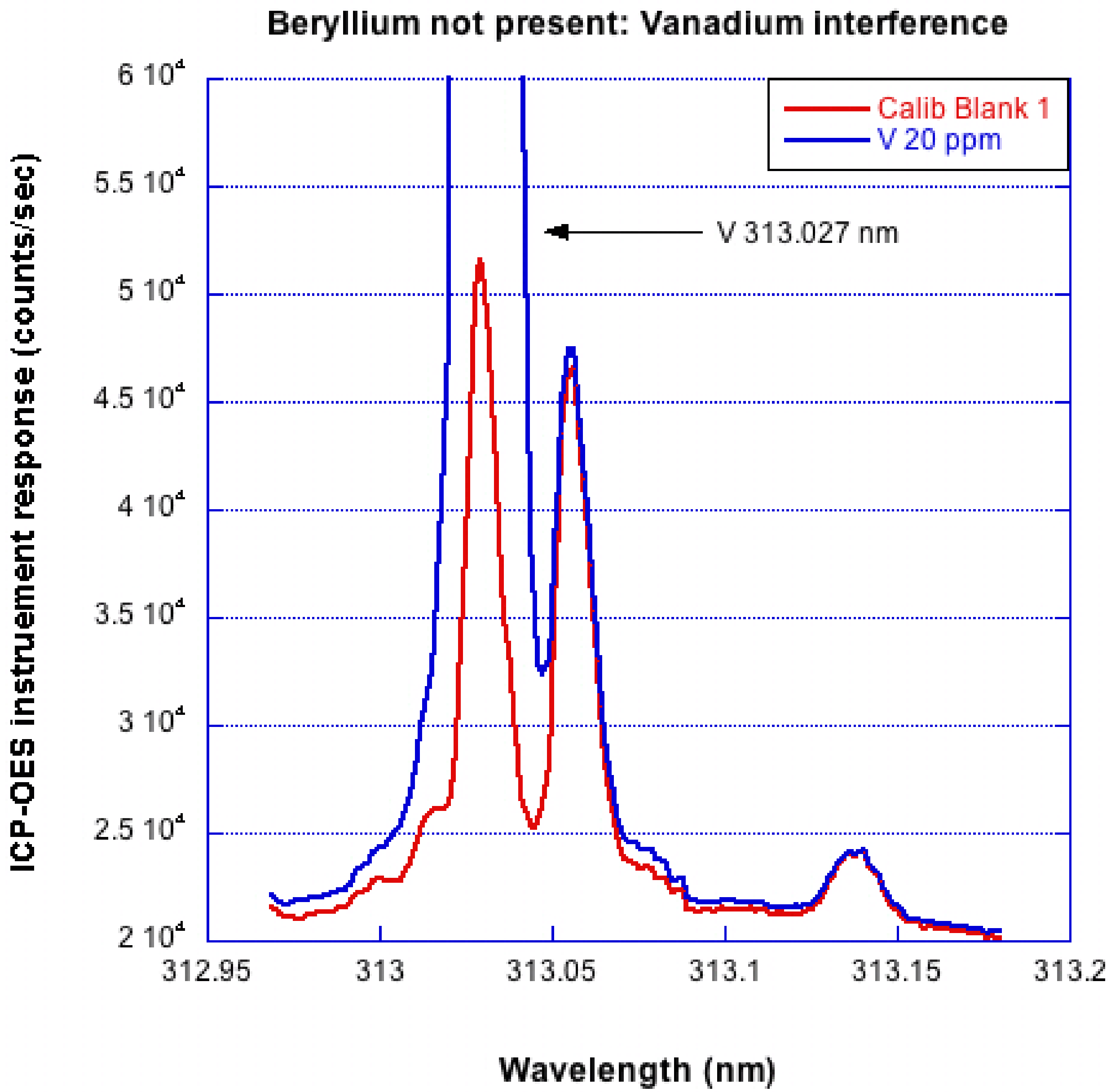
Major zirconium line does not interfere with beryllium peak



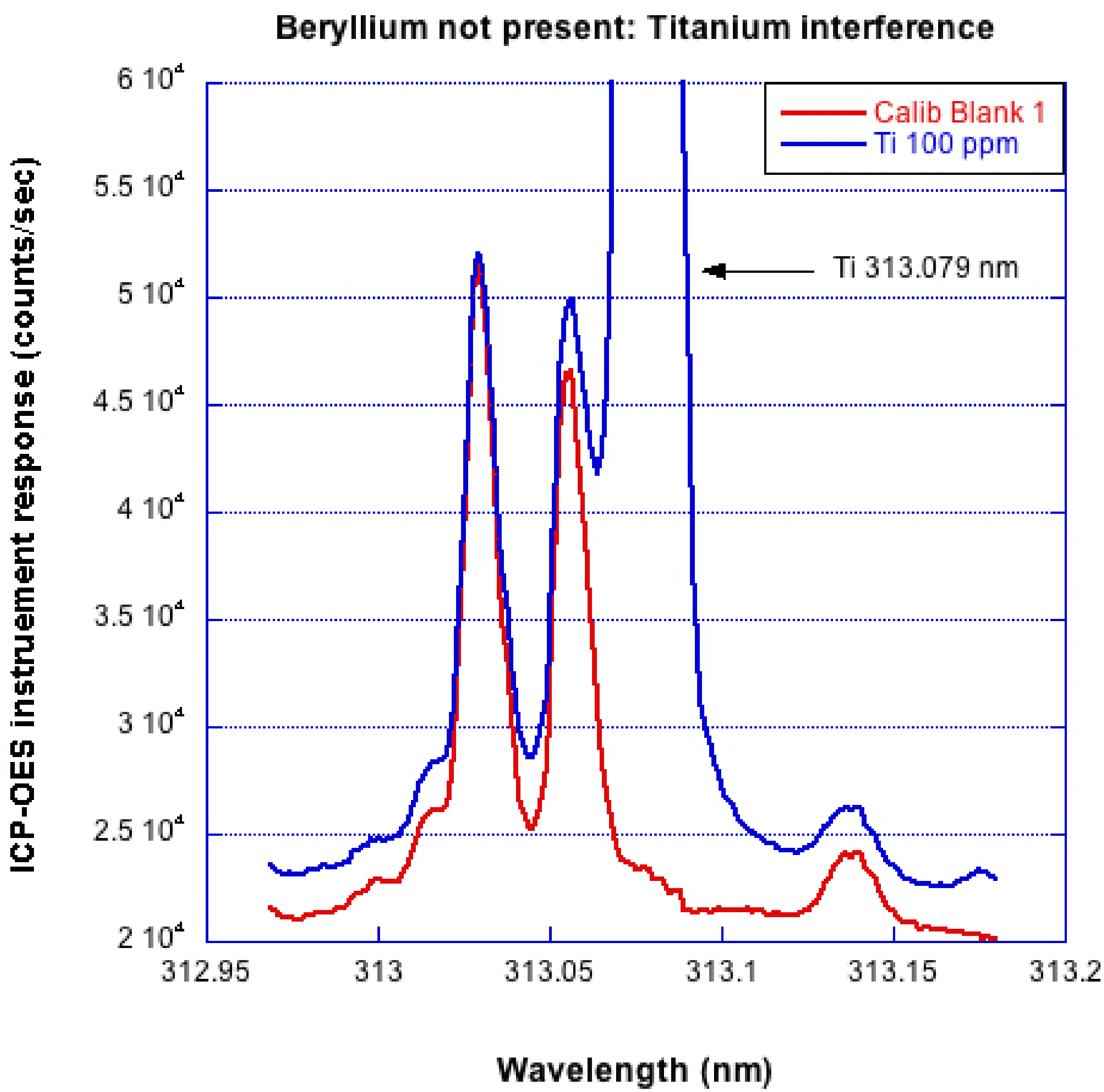
But direct overlap of minor Zr 313.111 nm peak



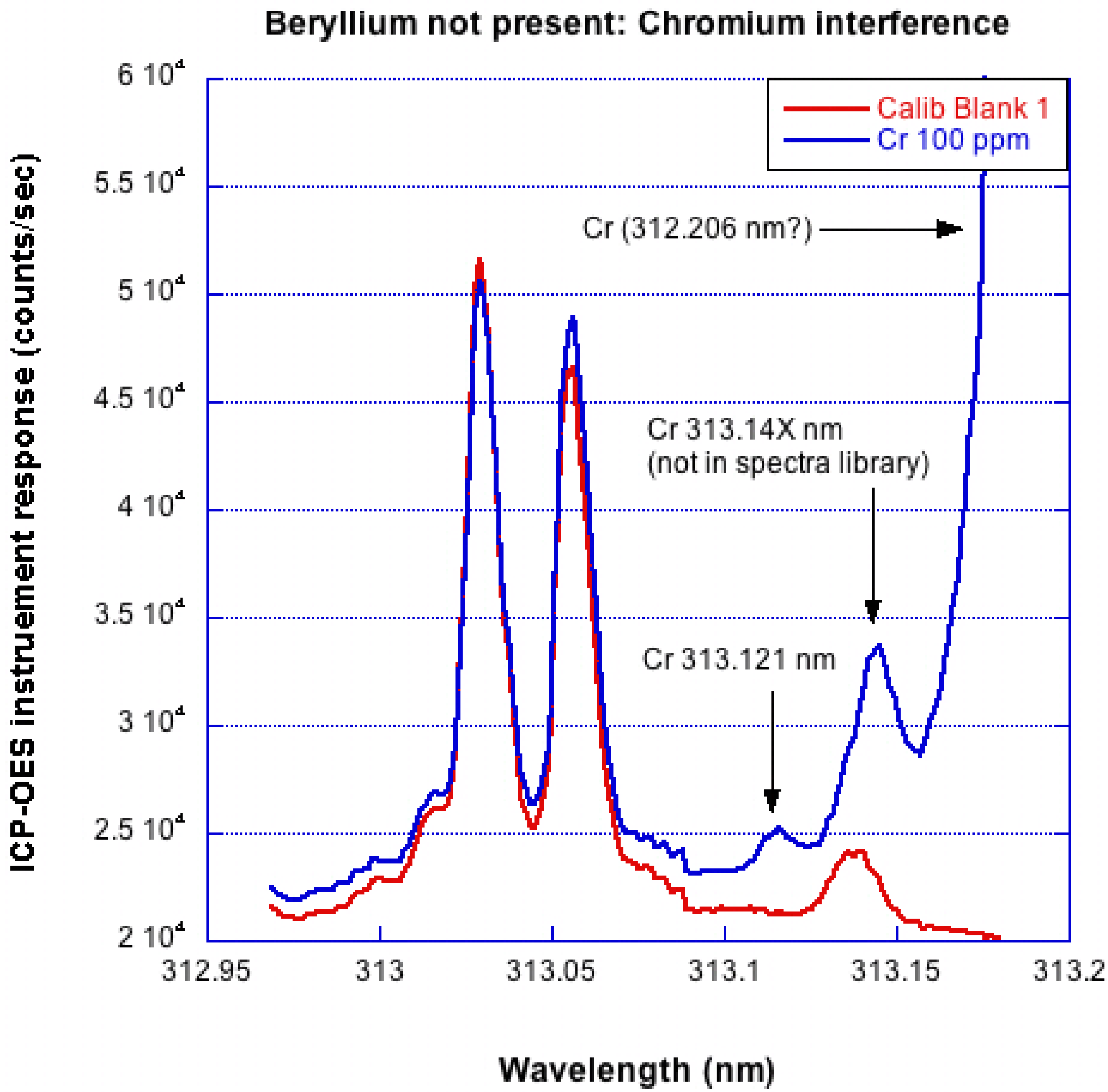
Vanadium line overlap on Be 313.042 nm peak position



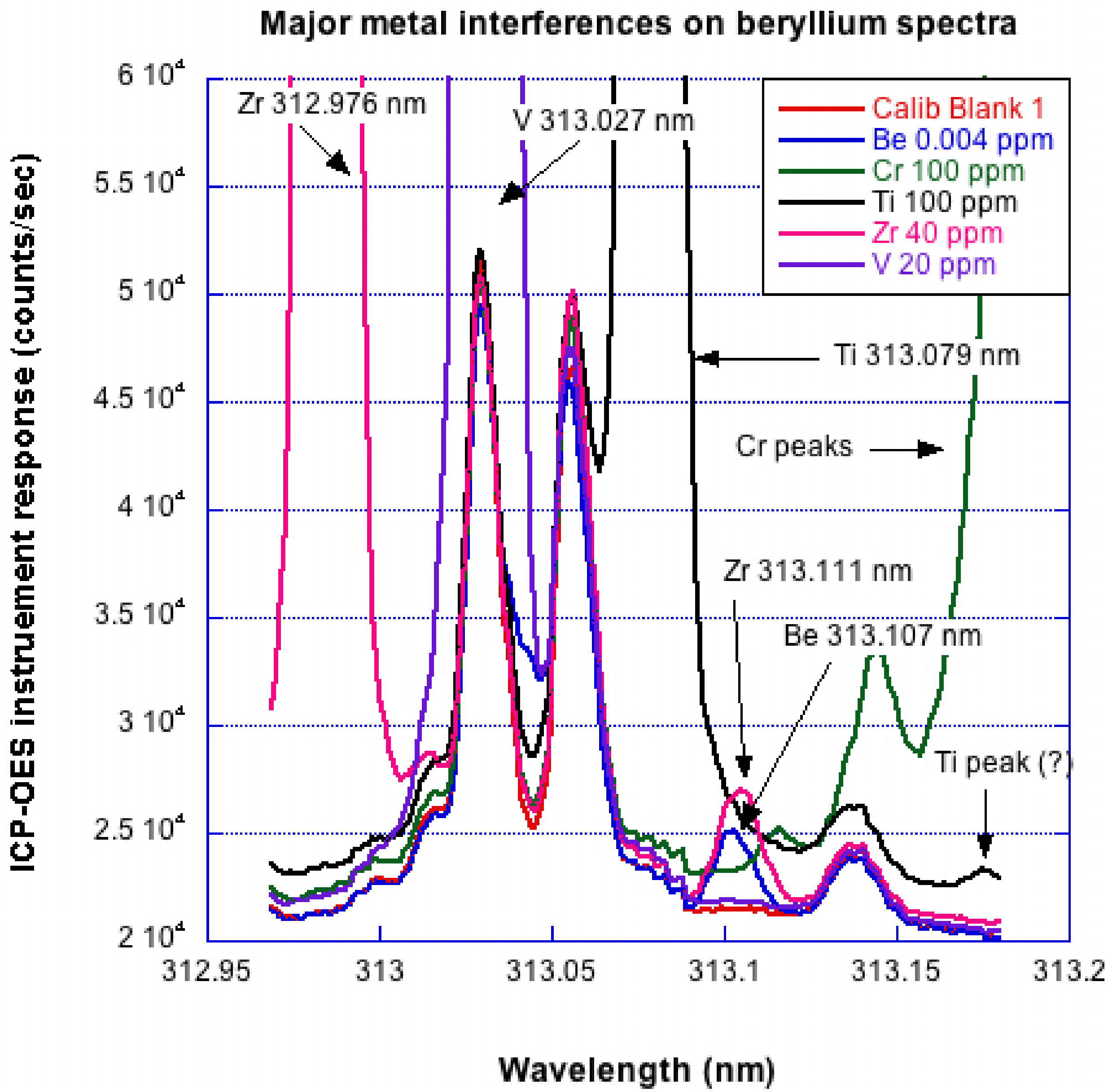
Titanium line overlap on Be 313.107 nm peak position



Chromium line overlap on Be 313.107 nm peak position



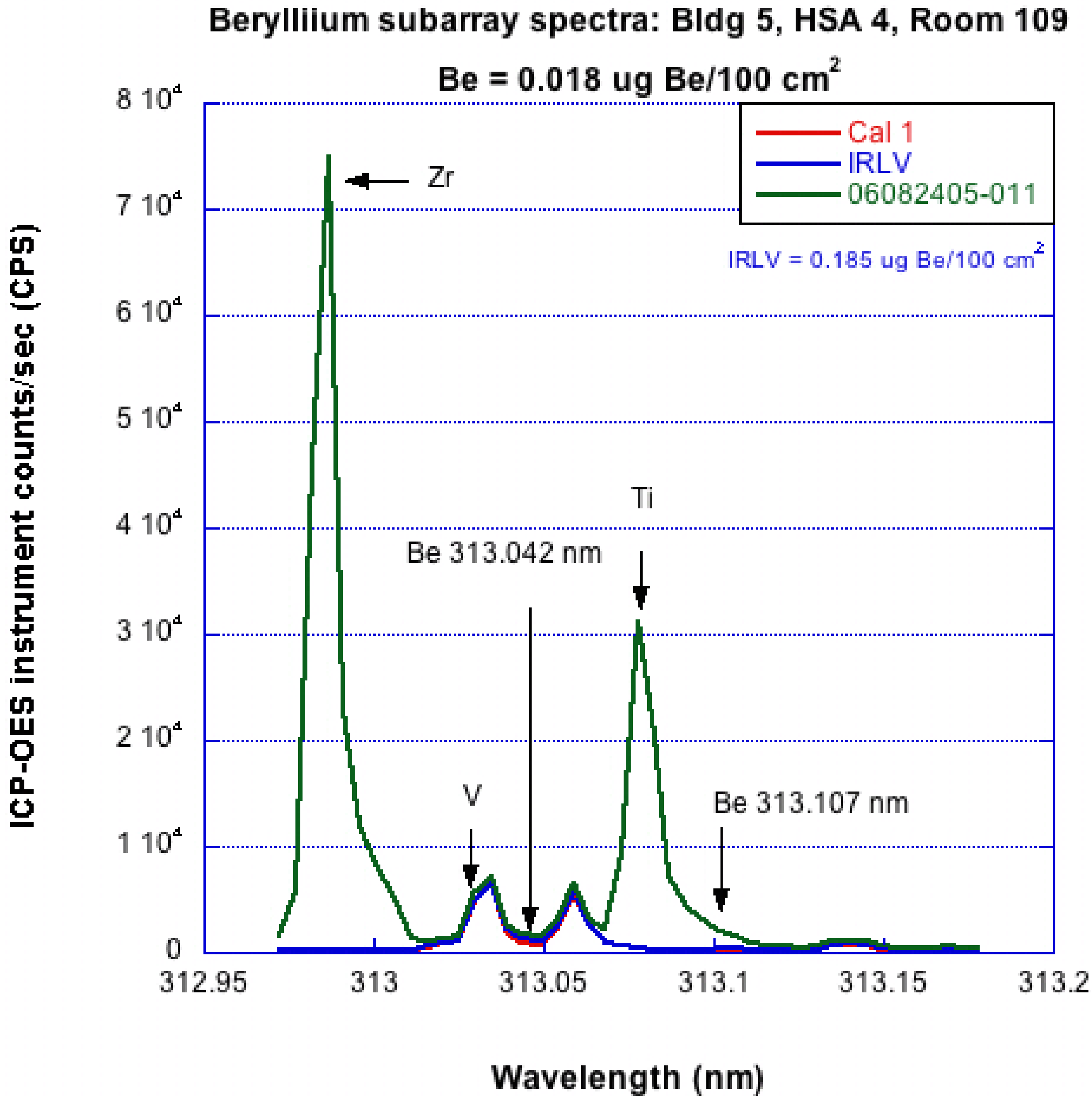
Sum of major interferences



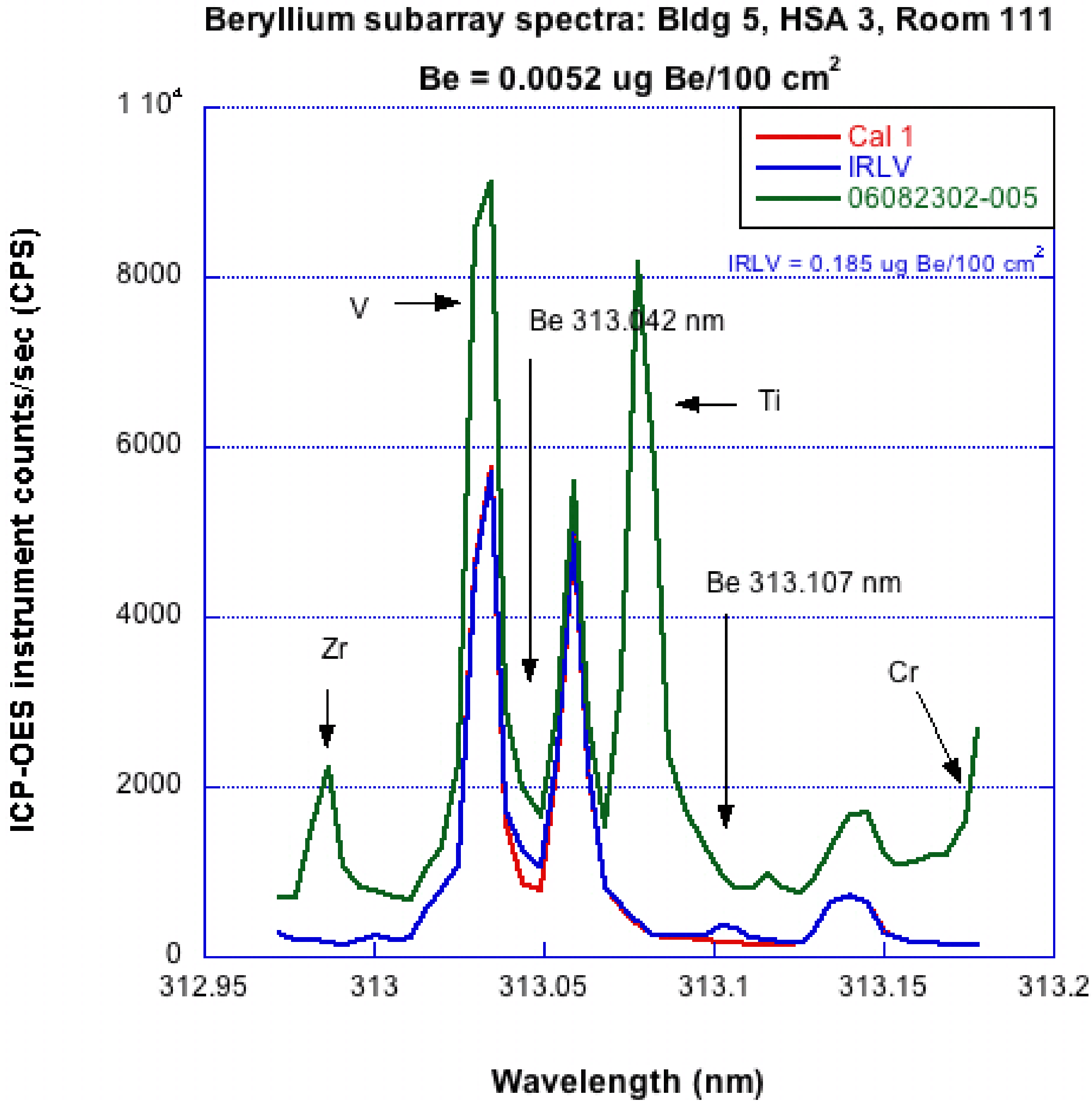
Examples of major spectral interferences in real world samples at the NETL-Albany site:

- High zirconium + titanium
- High vanadium and chromium + titanium
- High titanium
- Background soil
- Ceiling tile

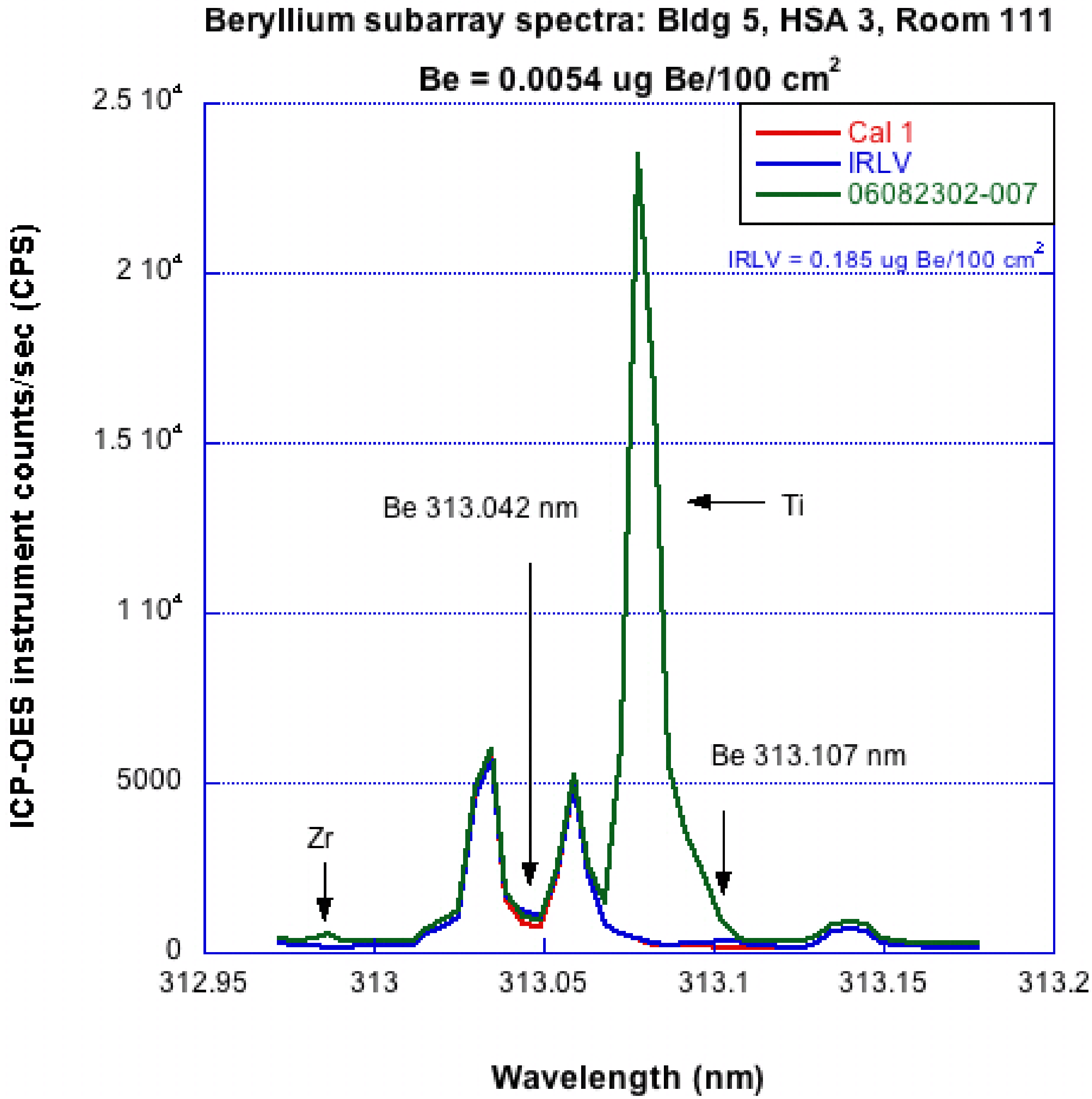
Wipe sample, high resolution mode (contractor lab)



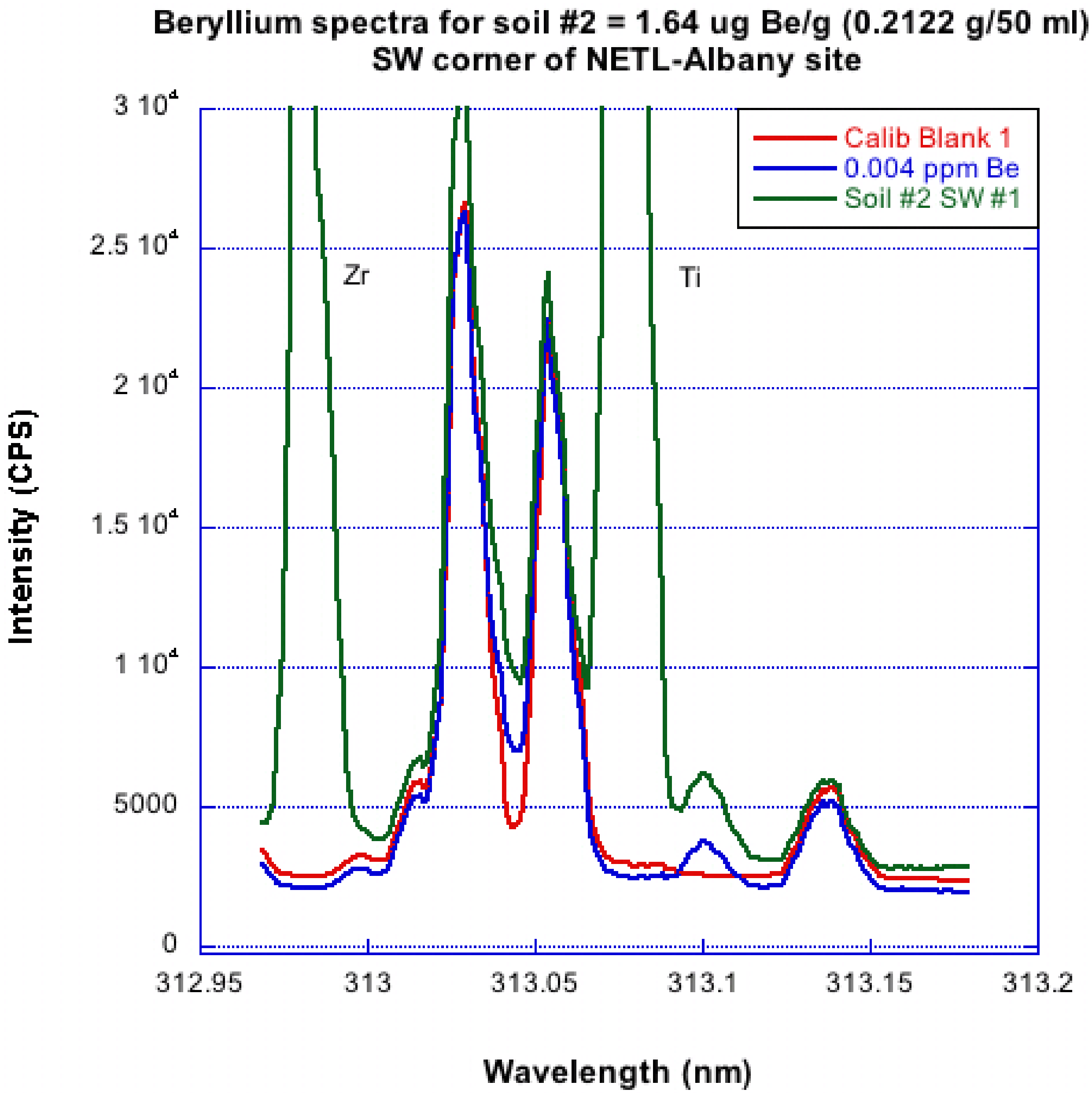
Wipe sample, high resolution mode (contractor lab)



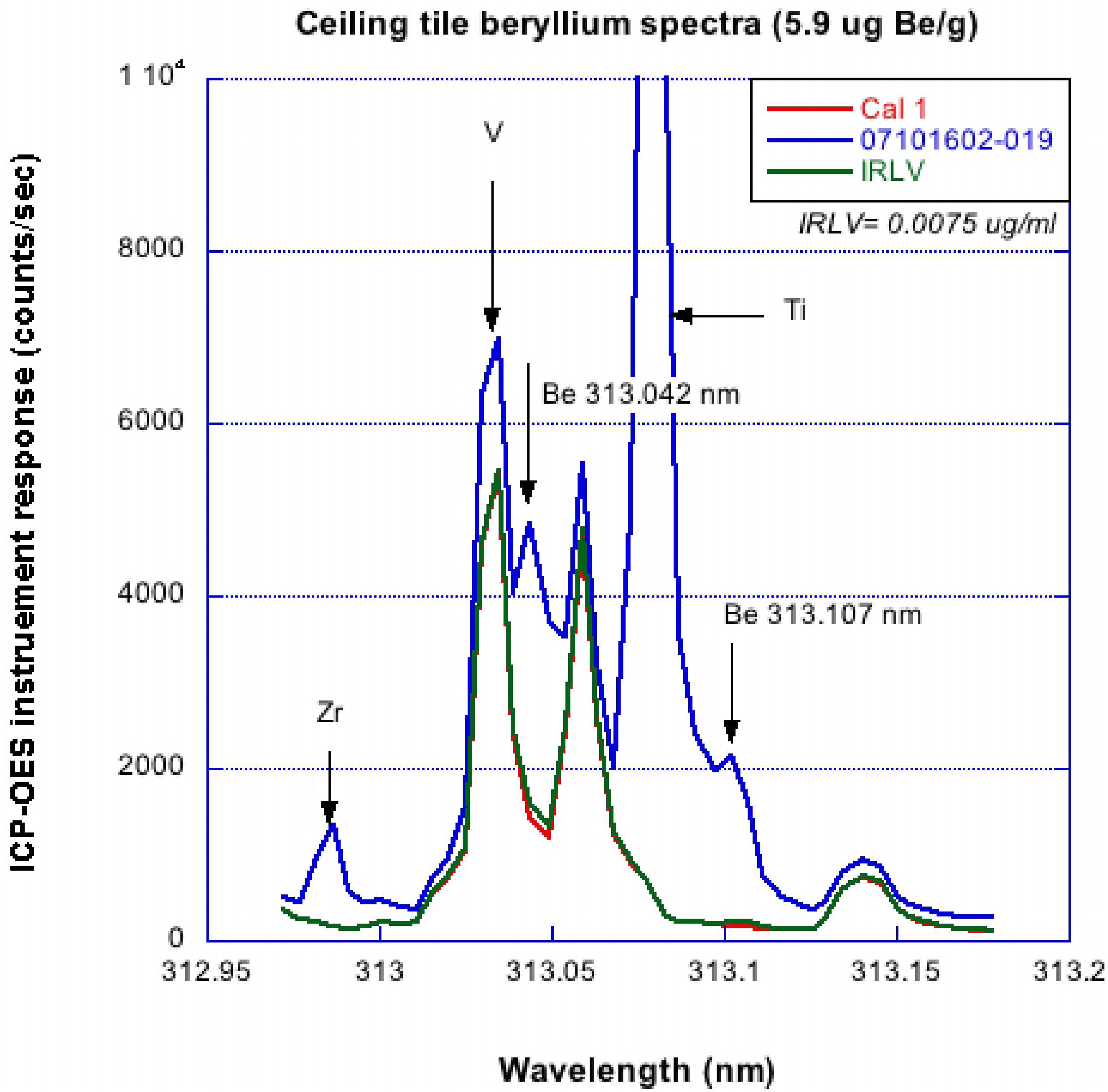
Wipe sample, high resolution mode (contractor lab)



Bulk soil sample, profile mode,144 pts/array (NETL-Albany)



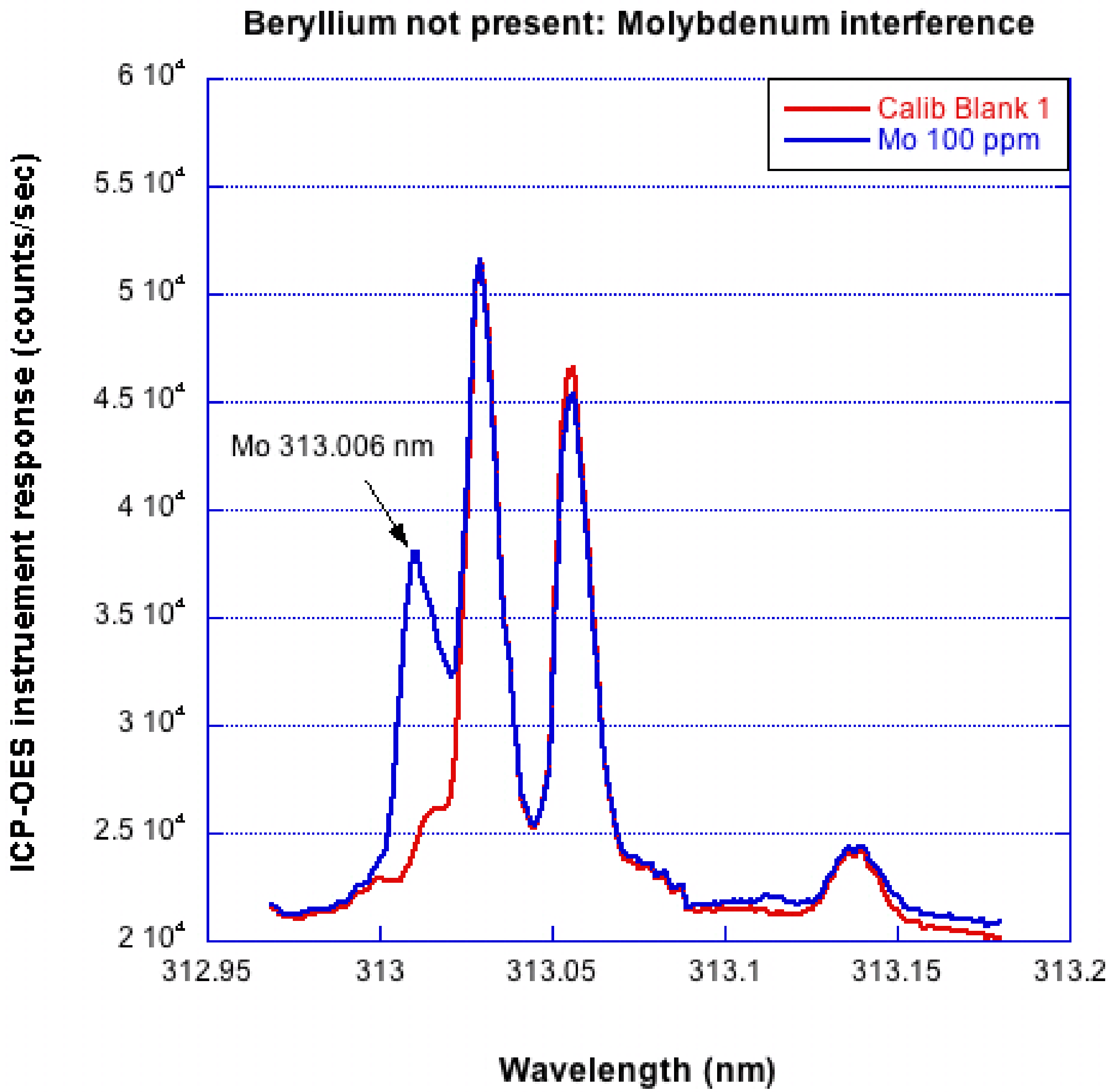
Ceiling tile beryllium source, possibly perlite (contractor lab)



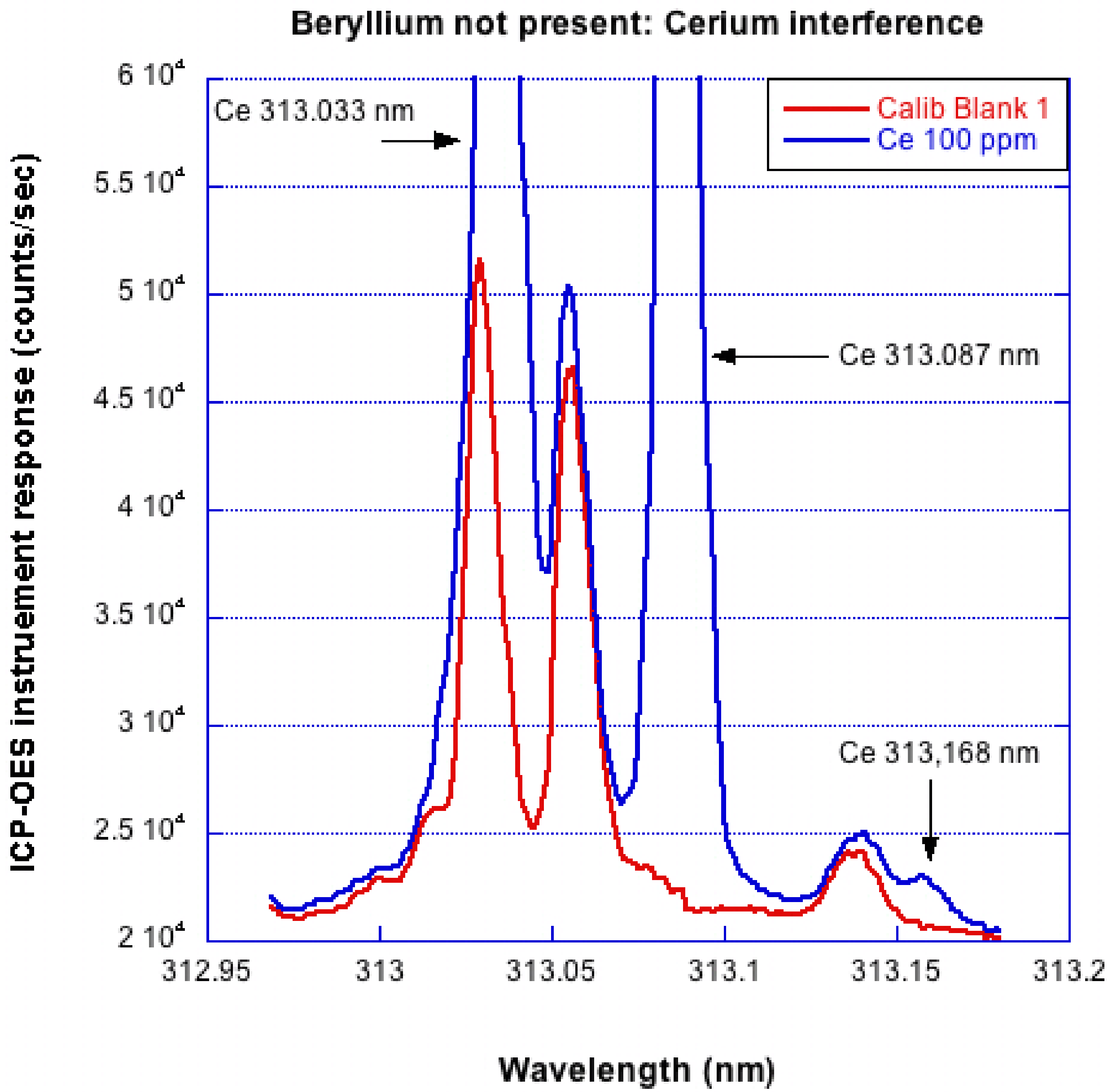
Uncommon spectral interference on beryllium 313.042 nm and 313.107 nm lines

Element	state	Wavelength (nm)
Molybdenum	?	313.006
Cerium	?	313.033 313.087 313.168
Niobium (Columbium)	II	313.079
Thulium	II	313.126

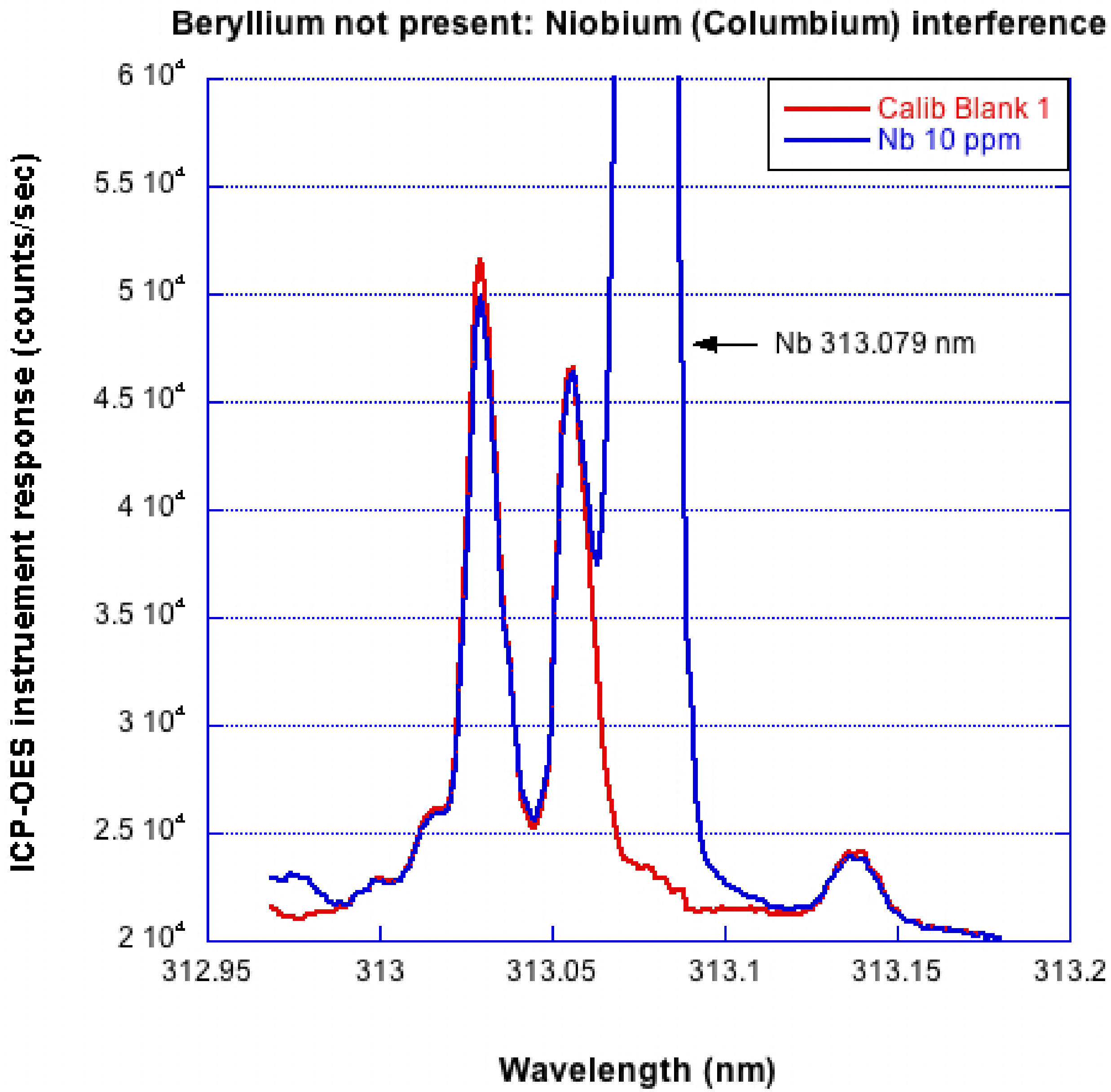
Molybdenum interference on Be 313.042 nm position



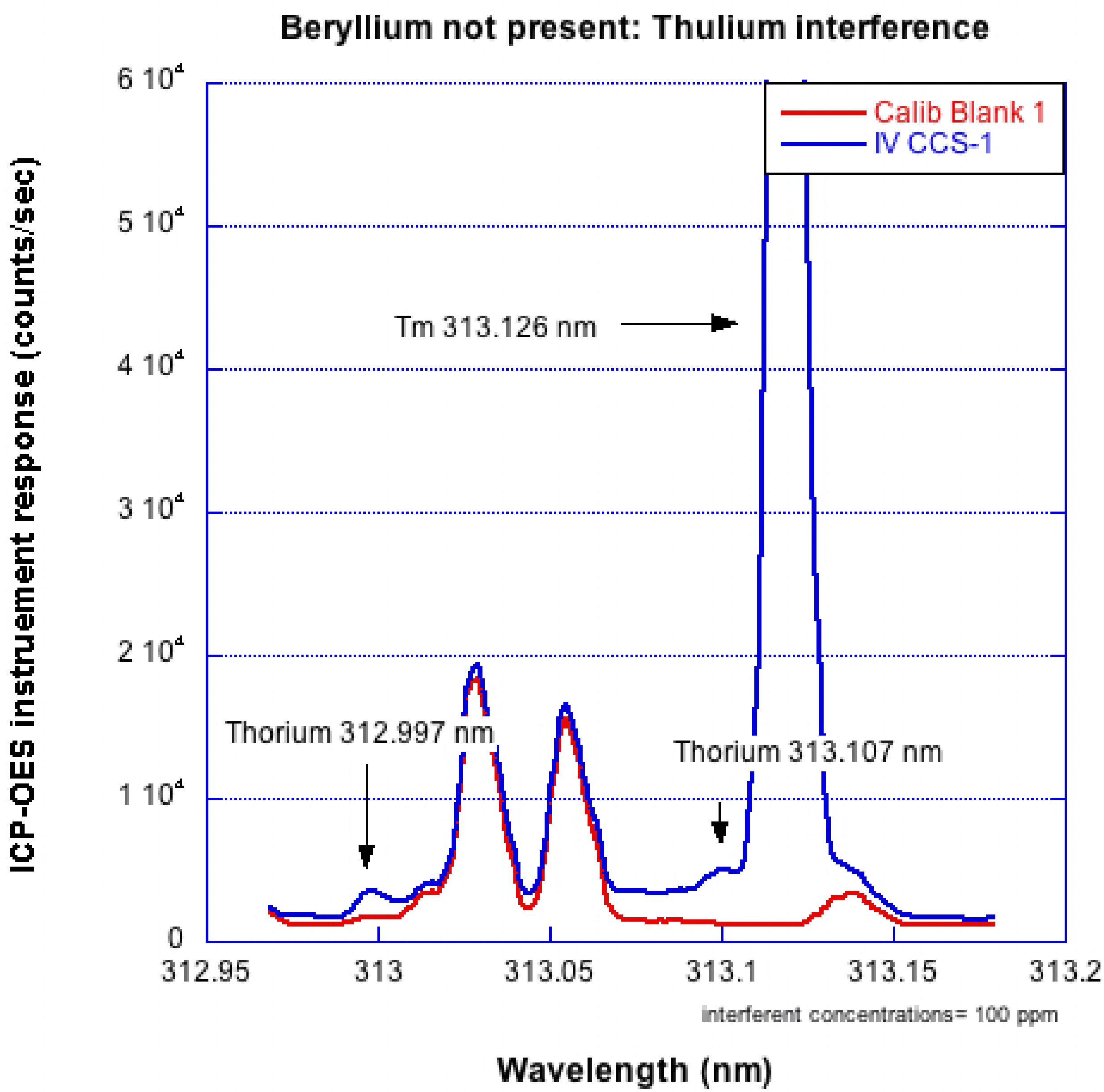
Cerium interferences on both Be line positions



Niobium interference on Be 313.107 nm position



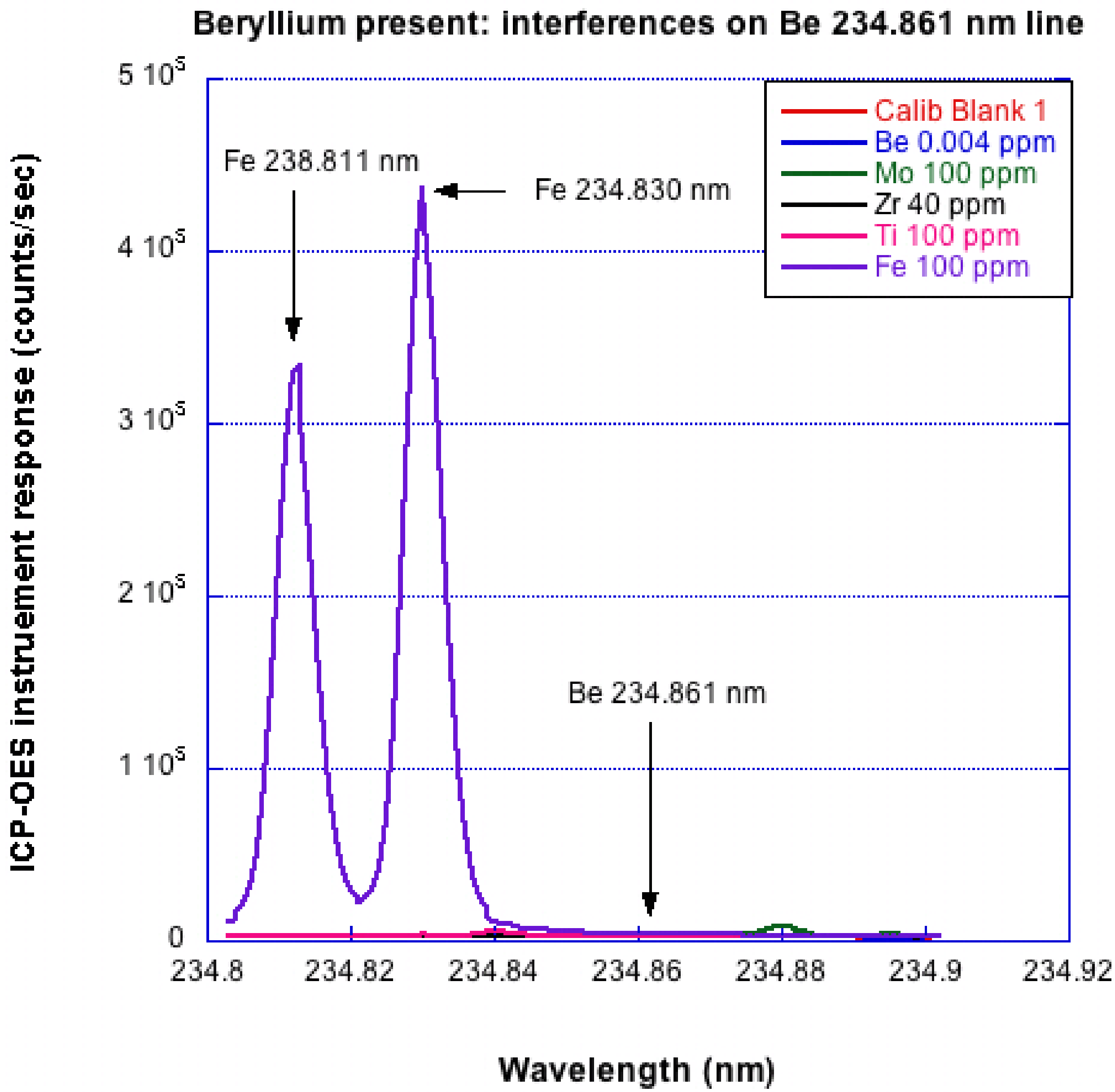
Thulium interference on Be 313.107 nm position



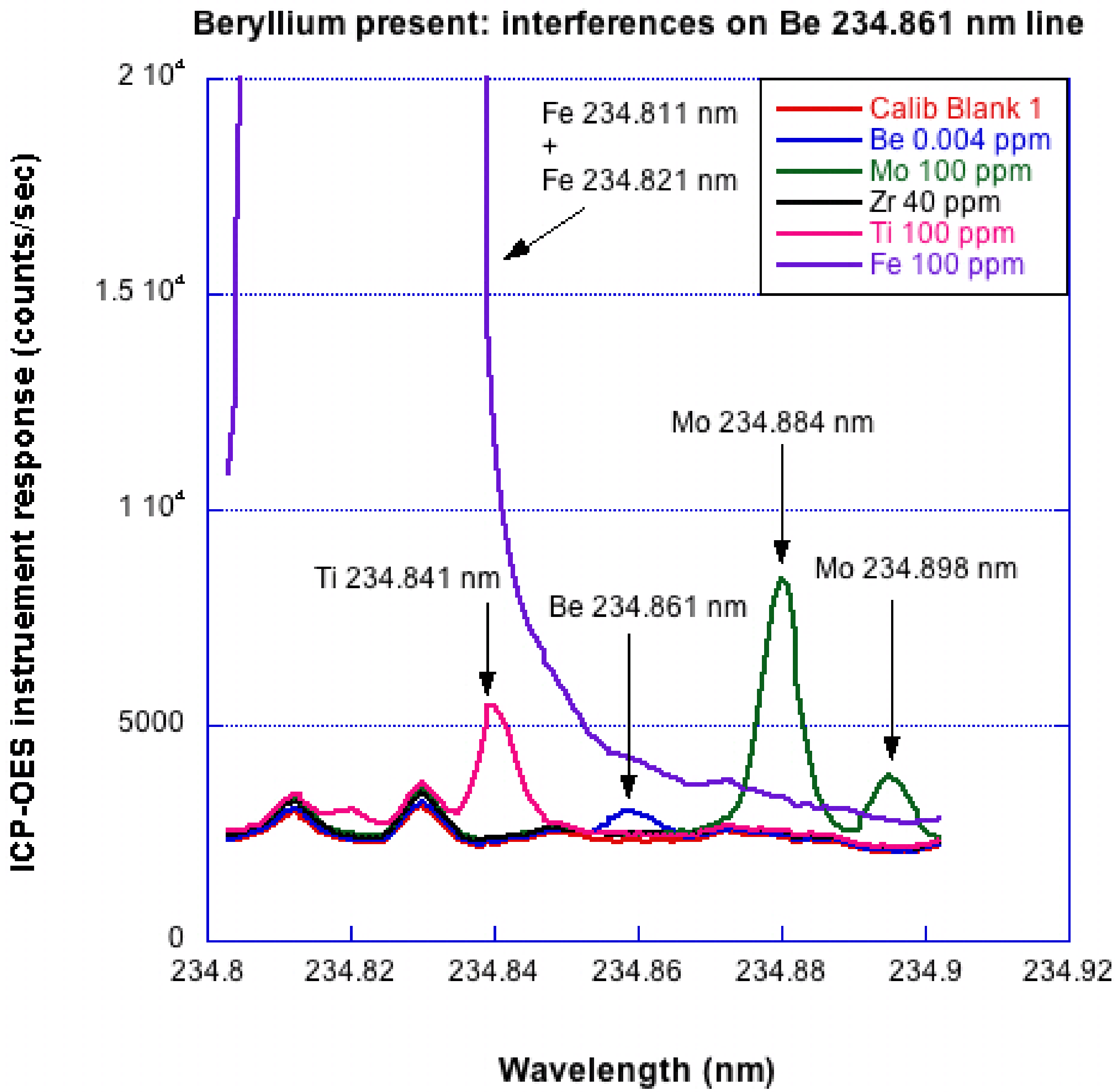
Spectral interferences on the alternative beryllium 234.861 nm line

Element	state	Wavelength (nm)
Iron	?	313.006
Molybdenum	?	313.033 313.087 313.168
Titanium	II	313.079

Intense iron peaks and the Be 234.861 position



Iron interference on Be 234.861 nm position



Negative measurement bias due to interferences

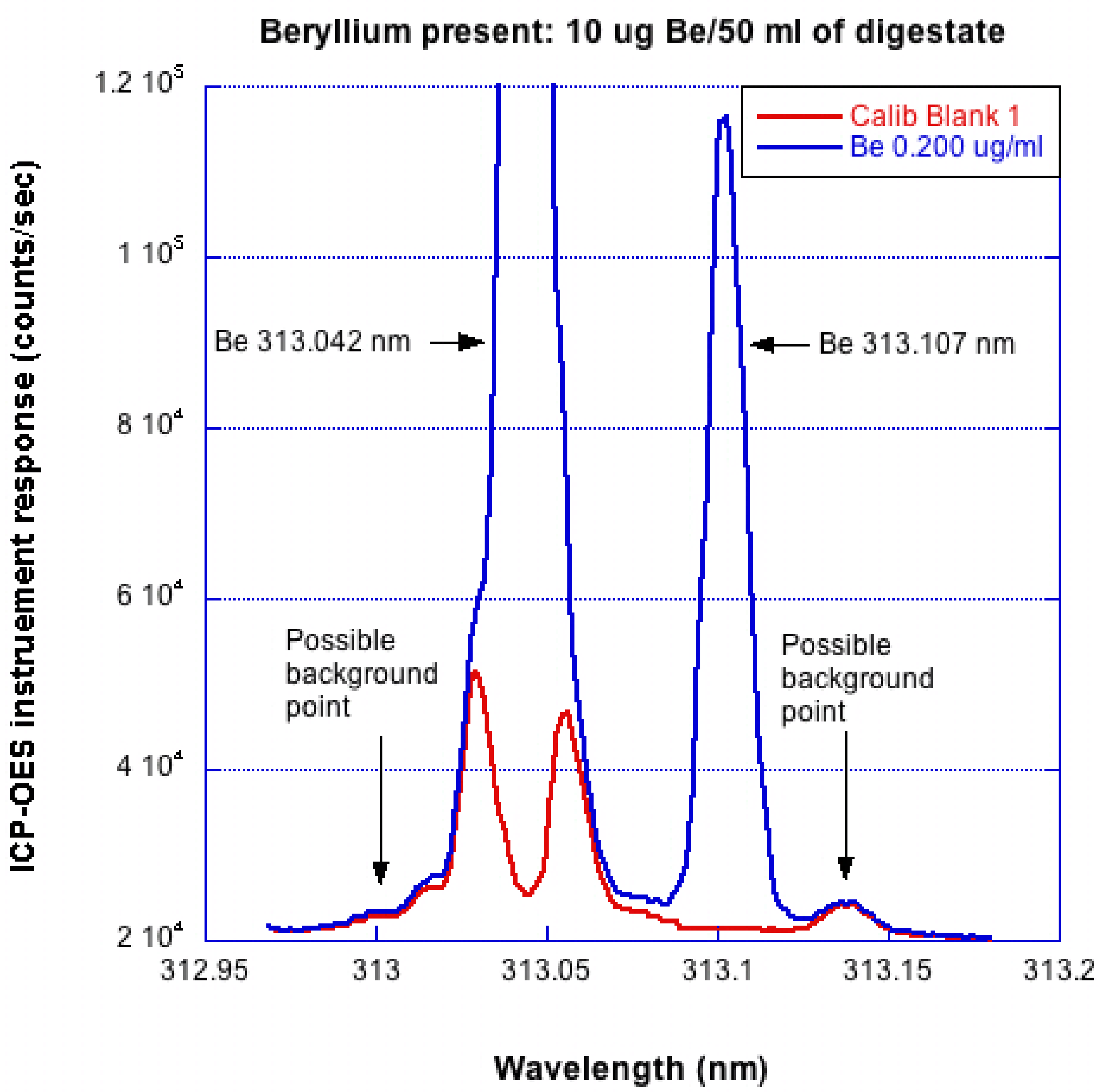
	Beryllium is present	Beryllium is absent
Detected	**Correct decision**	**Incorrect Decision: False Positive (Type I error)**
Not detected	**Incorrect decision: False Negative (Type II error)**	**Correct decision**

Negative bias results from an interference peak on top of the chosen background point

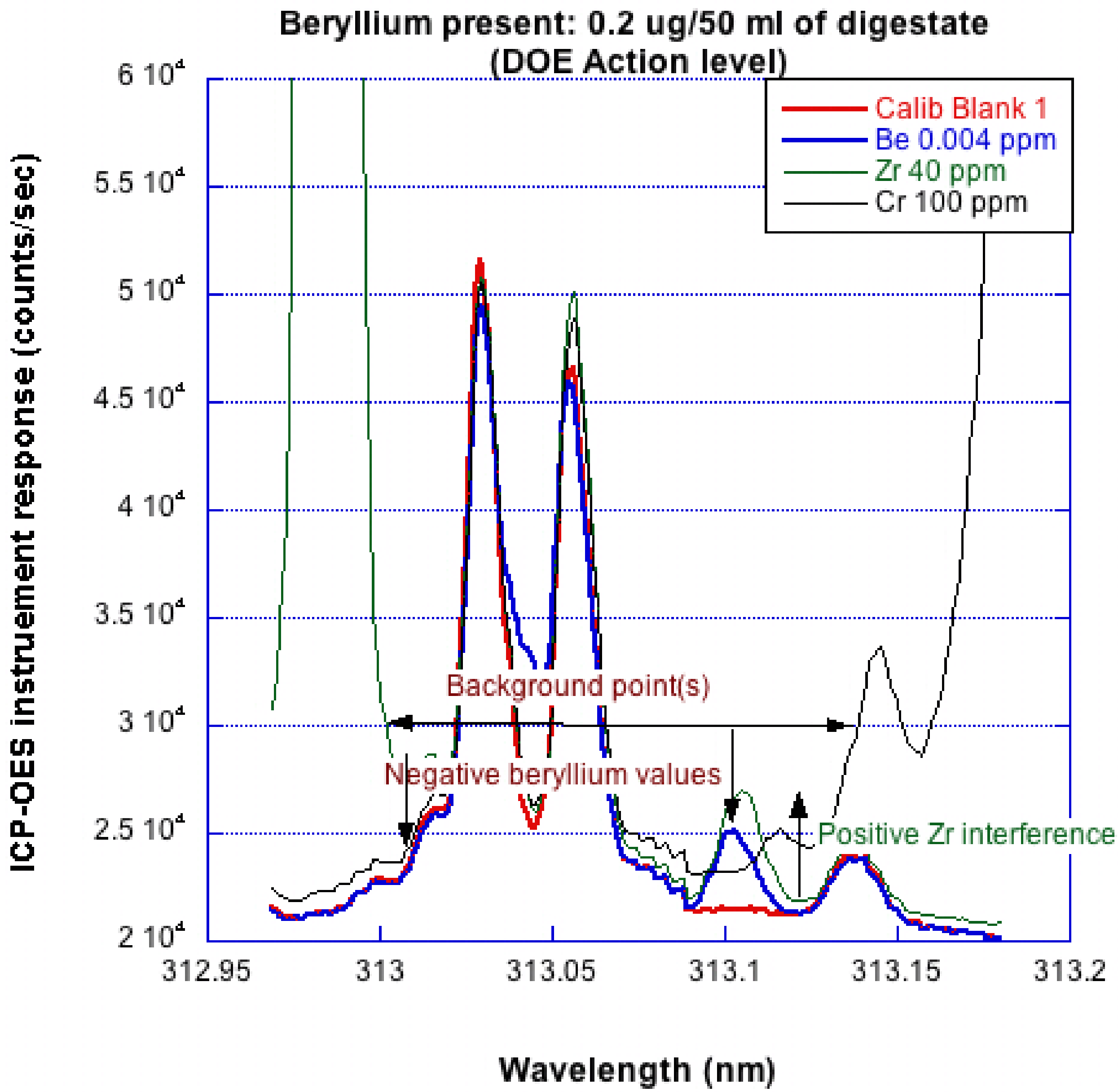
Common when using classical background correction methods:

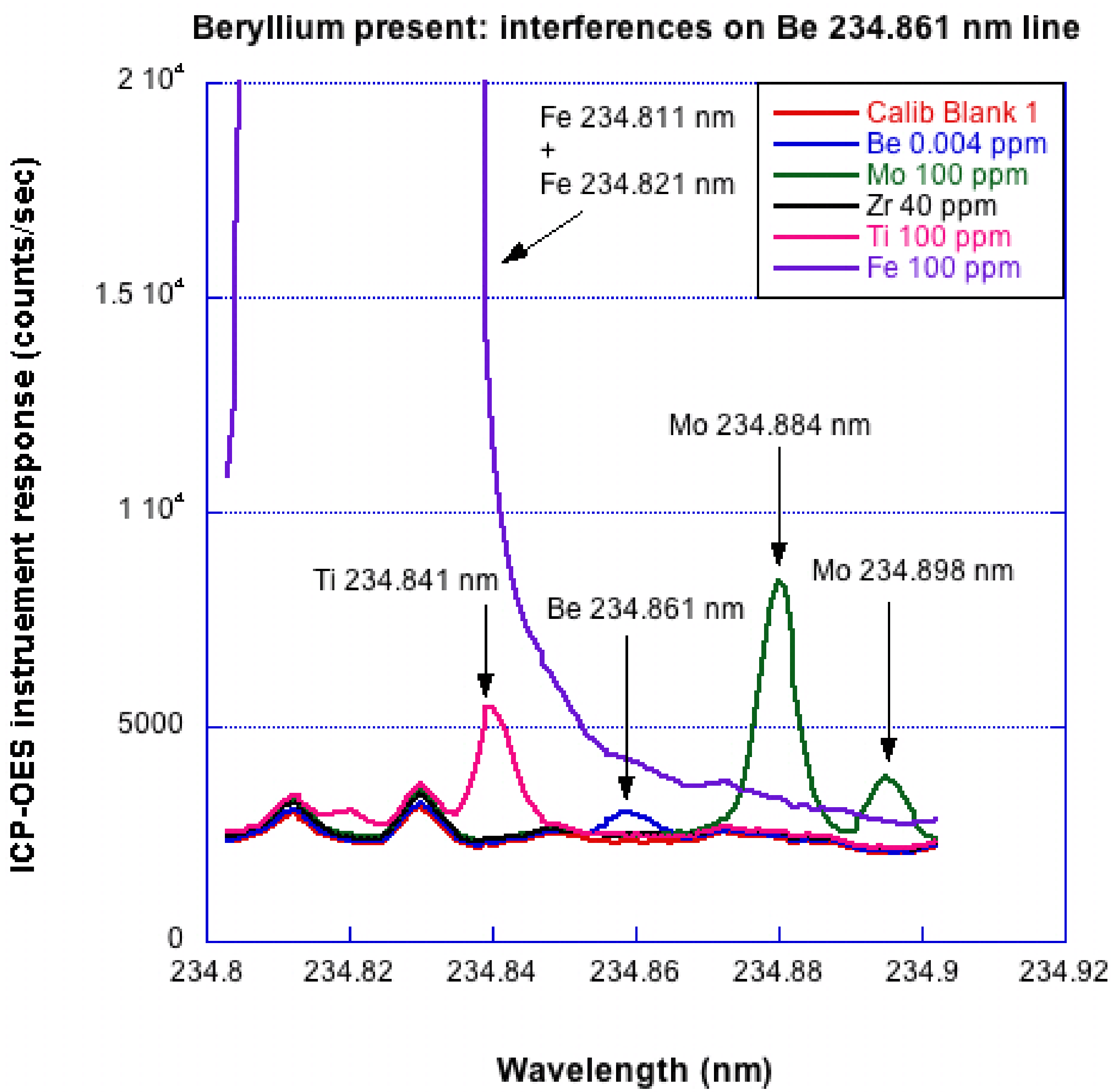
- **Peak area**
- **Peak height**

- **Inter-Element Corrections (IECs)**



Beryllium present: 10 ug Be/50 ml of digestate
Calib Blank 1
Be 0.200 ug/ml
Be 313.042 nm
Be 313.107 nm
Possible background point
Possible background point
ICP-OES instruement response (counts/sec)
Wavelength (nm)
1.2 10^5
1 10^5
8 10^4
6 10^4
4 10^4
2 10^4
312.95
313
313.05
313.1
313.15
313.2


Beryllium present: 0.2 ug/50 ml of digestate
(DOE Action level)
Calib Blank 1
Be 0.004 ppm
Zr 40 ppm
Cr 100 ppm
Background point(s)
Negative beryllium values
Positive Zr interference
ICP-OES instruement response (counts/sec)
Wavelength (nm)
6 10⁴
5.5 10⁴
5 10⁴
4.5 10⁴
4 10⁴
3.5 10⁴
3 10⁴
2.5 10⁴
2 10⁴
312.95
313
313.05
313.1
313.15
313.2


Beryllium present: interferences on Be 234.861 nm line
ICP-OES instruement response (counts/sec)
Wavelength (nm)
2 10⁴
1.5 10⁴
1 10⁴
5000
0
234.8
234.82
234.84
234.86
234.88
234.9
234.92
Calib Blank 1
Be 0.004 ppm
Mo 100 ppm
Zr 40 ppm
Ti 100 ppm
Fe 100 ppm
Fe 234.811 nm
+
Fe 234.821 nm
Mo 234.884 nm
Mo 234.898 nm
Ti 234.841 nm
Be 234.861 nm

Photomultiplier detectors a barrier to using multivariate analysis methods

Detector type	Resolution (nm)
Photomultipliers (1980-1990s instruments)	0.030-0.050 (30-50 pm)
Charged coupled device (CCD) or charge injection device (CID) (1993-present)	
Low resolution	0.0096 (9.6 pm)
High resolution	0.0048 (4.8 pm)
Profile mode	0.0012 (1.2 pm)

Advantages of multicomponent spectral deconvolution techniques for beryllium

- **Combines spectral data information from both beryllium doublet peaks (313.042 and 313.107 nm)**

  (Comparable to Haaland et al. 1999 multi-window multivariate method)
- **Eliminates the need for spectrally clean background correction point(s).**
- **Uses more spectral information (44-176 pts) compared to peak area or IECs which:**
  - Decreases statistical error
  - Increases reproducibility
  - Reduces detection limits
  - Eliminates most negative (type II error) beryllium values
  - Residual plots serves as a quality assurance check.

Multi-component Spectral Fitting (MSF) process

(1) Collect model spectra of interferences, blank, and calibration standard for spectral regions of interest.

(2) Subtract blank from each single-element spectra to yield net spectra.

(3) Rescale each net spectra in until the spectrum is a best fit agreement with the measured spectrum.

(4) The scaling “factors” are then used for the concentration quantification for the analyte of interest.

Differences between PerkinElmer and NETL-Albany MSF model approaches

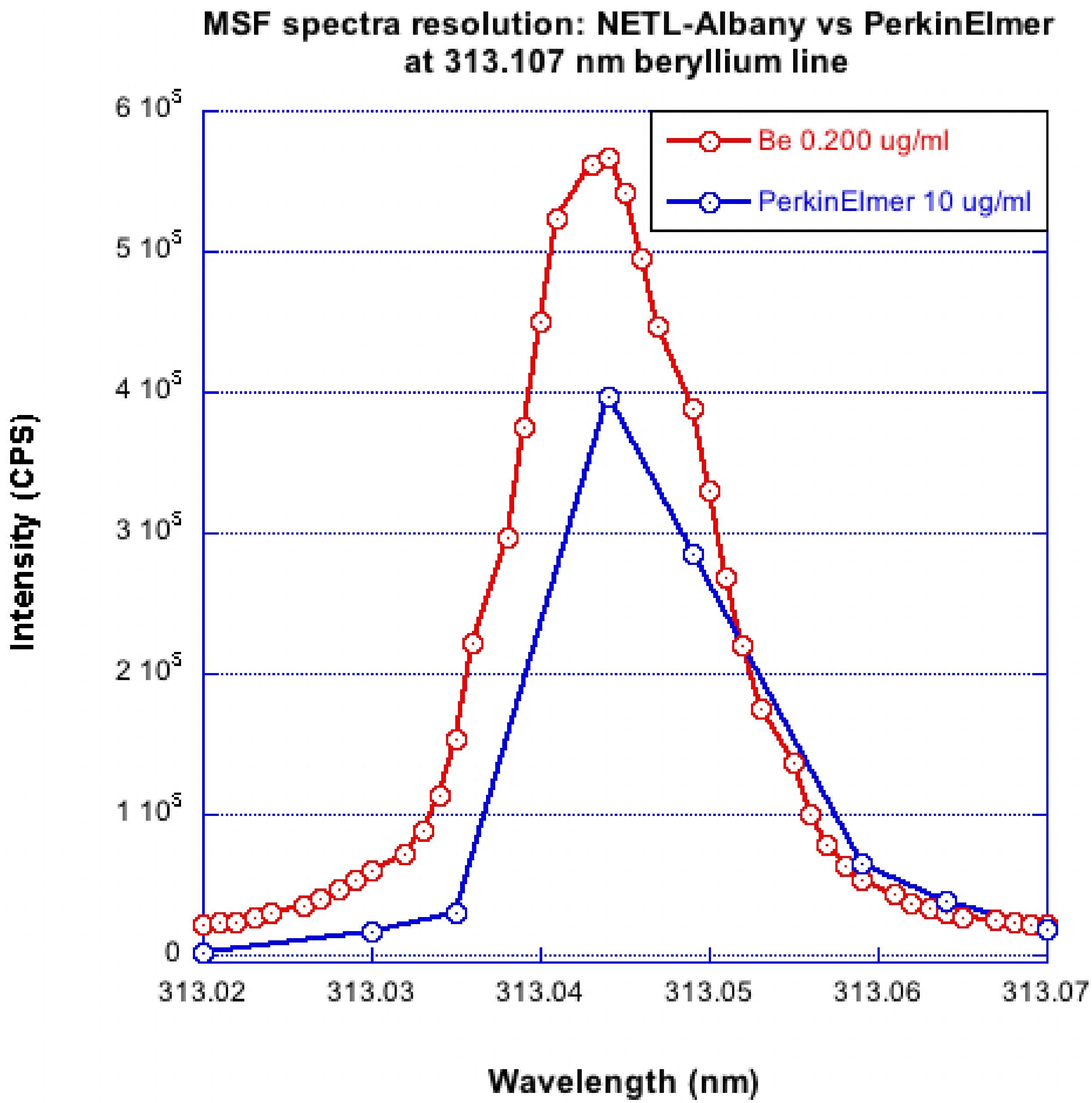
PerkinElmer	NETL-Albany
Collect data in high resolution mode. (44 data pts / Be 313 array)	Collect data in profile (scanning) mode. (176 data pts / Be 313 array)
Collect spectra for model once every about 6 month.	Collect spectra for model within each run.
Reuse MSF spectra model for each additional batch.	Create model each batch and post-process data.
Shorter sample read times.	4-times longer read times required by stepping a mirror.

NETL

Advantages of the NETL-Albany MSF approach

- Increased sensitivity (custom sample introduction system).
- Reduction in spectral noise via 4-times more points.
- More accurate spectra representation.
- Elimination of plasma temperature variations due to poorer RF coupling of plasma as the quartz torch undergoes vitrification over several months.

Beryllium spectra resolution and sensitivity



Accuracy and precision comparison for between-batch check standards

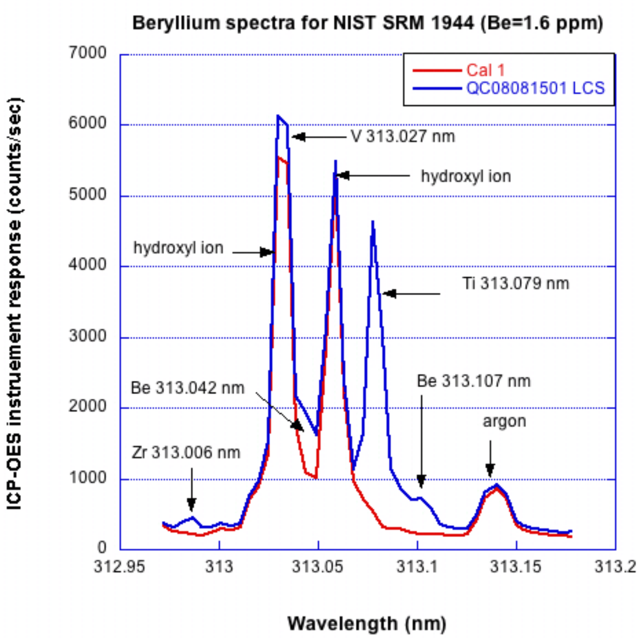
Data Quality	Perkin Elmer MSF method	NETL-Albany MSF method
Be concentration (ug/ml)	0.0075 ug/ml (0.188 ug/25 ml)	0.0040 ug/ml (0.2 ug/50 ml)
Average measured conc. (ug/ml)	0.0078	0.0041
Percent bias	4	2.5
%RSD	8.1	3.7
# of sample batches	75	16

NETL

Instrument detection limit comparisons

Data Quality	Perkin Elmer MSF method	NETL-Albany MSF method
Sample ran	DDI water blank	0.0004 ug/ml sample
True instrument detection limits	0.0078 ug/sample N=21 0.0015 ug/100 cm2 (514 cm2 wipe area)	0.0028 ug/sample %RSD= 6% N=18 0.0006 ug/100 cm2 (514 cm2 wipe area)

Between batch Standard Reference Material recovery using the PerkinElmer MSF method



- **NIST SRM 1944 reference beryllium value = 1.6 ug/g**
- **Average beryllium recovery = 1.56 ug/g**
- **%RSD= 6.4%**
- **Number of batches = 75**

NETL-Albany beryllium %recoveries (Sample reps=4, %RSD 0.3-2.8)

Reference material	EPA 3050B (Sc=5.0 ppm)	USGS (Lu=1.0 ppm)
JA-2	**92**	**90**
JB-1a	**92**	**91**
JR-2	**93**	**80**
JG-2	**94**	**86**
NBS 1646	**107**	**113**
NBS 1633a	**97**	**91**
NIST 2704	**98**	**106**
NIST 2709	**102**	**129**
NIST 2710	**83**	**81**
NIST 2711	**87**	**85**
CCRMP SY-2	**101**	**97**
USGS GXR-3	**94**	**90**
JB-2	**86**	**126**
Average recovery	**95**	**95**

Reference beryllium values of selected international reference materials

Reference materials	Total Be (ug/g)	Tolerance range (ug/g)
JA-2	2.05	0.44
JB-1a	1.3	0.04
JR-2	3.75	0.54
JG-2	3.26	0.52
NBS 1646	1.5	-
NBS 1633a	12	-
NIST 2704	1.6	0.07
NIST 2709	3.7	-
NIST 2710	2.5	-
NIST 2711	2.2	-
CCRMP SY-2	22	-
DOI GXR-3	26	4
JB-2	0.26	0.043

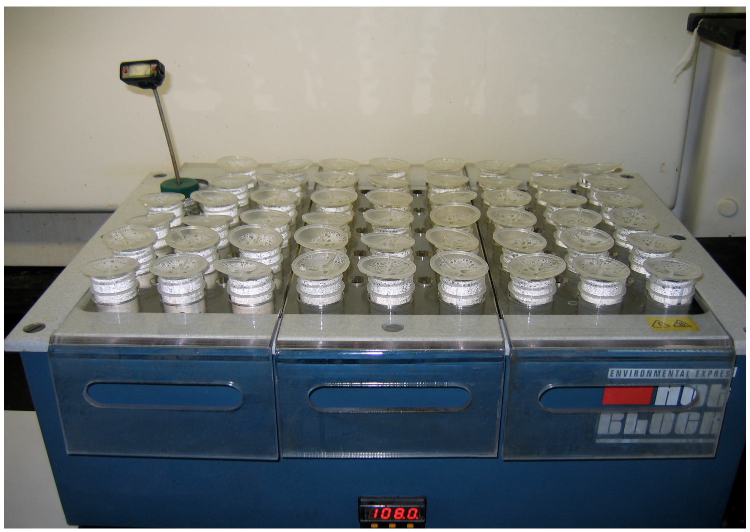
Suggested guidelines for the generation of single-element spectra

- Use high-purity single element solutions
- Ensure element concentrations are below the self-adsorption limit
- Collect data at the highest spectra resolution to maximize information (profile mode)
- Ensure complete element washout between collection of each individual spectra
- Collect all interferent spectra within each analysis batch
- Add appropriate pure internal standard(s) to all solutions- except the calibration blank.
- Clean sampling tubing with acid (1% HNO_3) prior to introducing blank standard.

Avoid potential sample processing errors

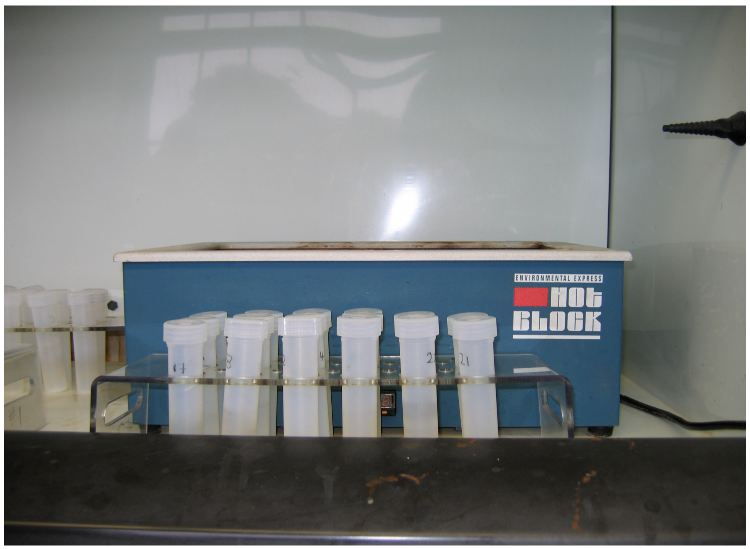
- Digestion
- autosampler and pump
- Nebulizer and spray chamber
- Injector and torch
- Plasma and RF coil
- Quartz optical window

Potential Bias: Hot-Block digestion 95C



- Incomplete beryllium recovery using 50% HNO3 digestion and NIOSH method 9102 for some beryllium species.
- Splattering losses with carbonate rich samples.
- Potential dust contamination.

Potential Bias: Hot-Block digestion 140C



- Splattering losses with carbonate rich samples.
- Long digestion time in USGS method increases potential dust contamination.
- Cross contamination from failure to run vessel cleanouts between runs.

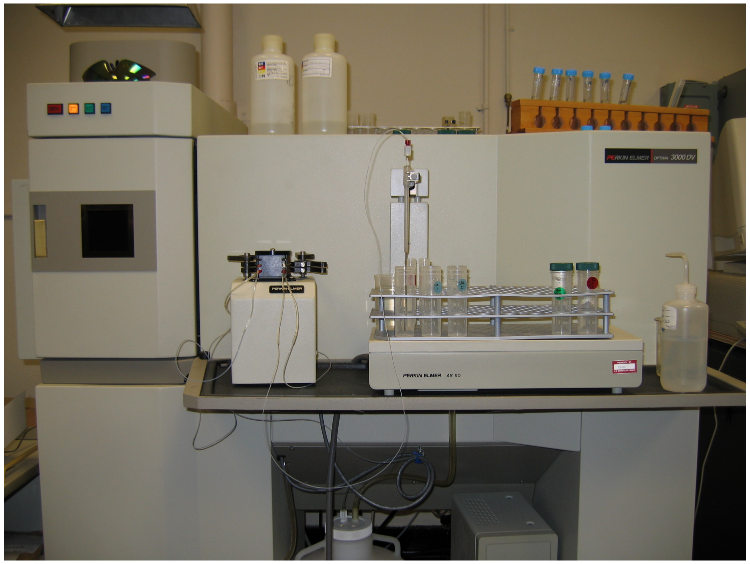
Potential bias: Microwave digestion

(used with permission from PerkinElmer)

- **Cross contamination from failure to run vessel cleanouts between runs.**
- **May require of ion-exchenge purification of boric acid to eliminate contamination in HF-HNO3-HCl-H3BO3 digestions.**

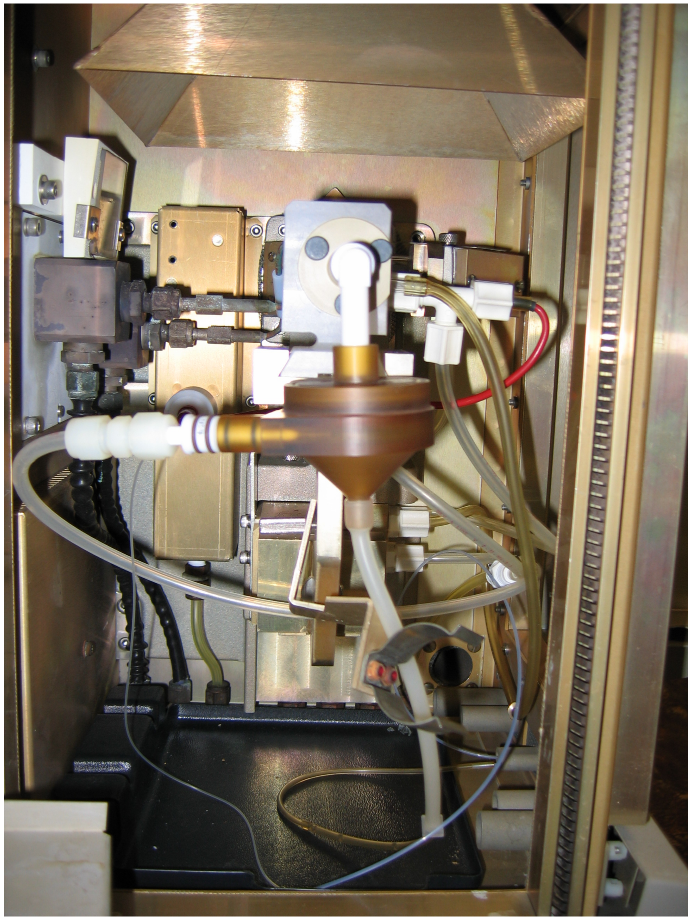
Note: High effectiveness of microwave digestion process makes this method preferable to static open digestions

Potential bias: Autosampler and pump



- Cross contamination from autosampler sipper probe
- Dust contamination
- Peristaltic pump noise
- Pump tubing wear

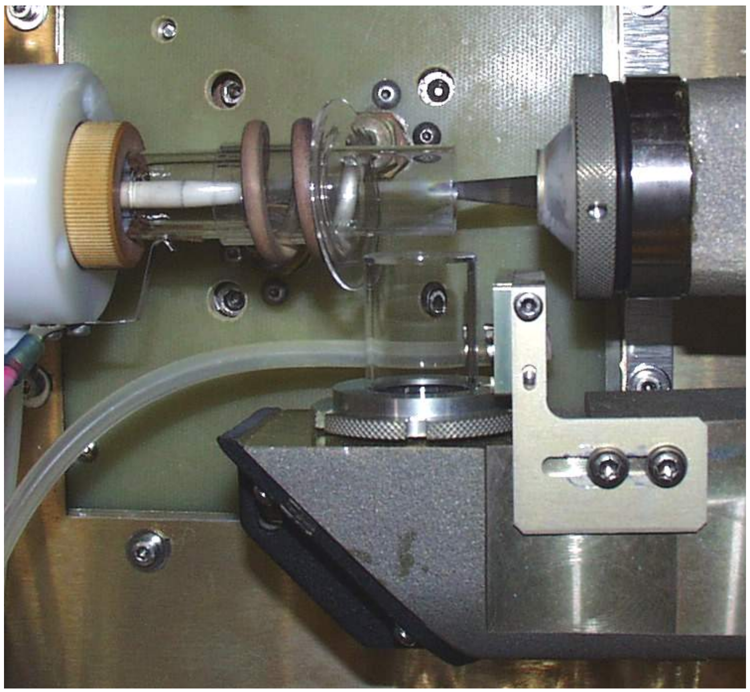
Potential bias: Customized nebulizer and spray chamber assembly



- Variation in nebulizer droplet size distribution resulting in changes in sample transport percentage to plasma
  (Solution: Bergener high-salts nebulizer)
- Lack of cyclonic spray chamber wetability
  (Solution: ULTEM high wettability spray chamber)

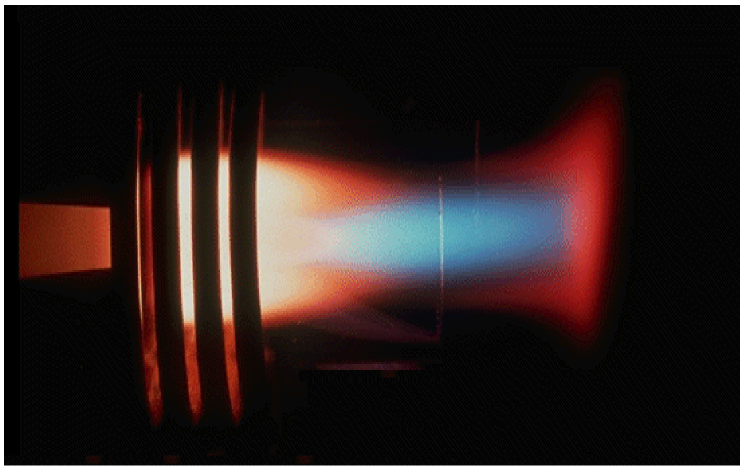
NETL

Potential bias: Injector/torch/RF coil
(used with permission from PerkinElmer)



- **Deposition and random release of contaminants from injector if auxillary argon flow set too high.**
- **Lower sensitivity and optical dispersion due to Quartz window fogging.**

Potential bias: Plasma, shear gas on
(used with permission from PerkinElmer)



- Measurement of cooler plasma if air curtain set too far from plasma.
- Poor RF coupling due to vitrification of torch
- Poor RF coupling due to pitting of water cooled RF coil

Internal standards as a solution to most sample processing errors

Corrects for:

- Digestion losses
- Dilution errors
- Pump noise
- Sample transport efficiency to plasma
- Plasma noise

Criteria for choosing an internal standard

- Low concentration in analyzed samples
- Free of spectral interferences
- High spectral intensity
- Stable in the sample matrix

Suggested internal standards

- **Scandium (361.383 nm) at 5 ppm for samples low in scandium**

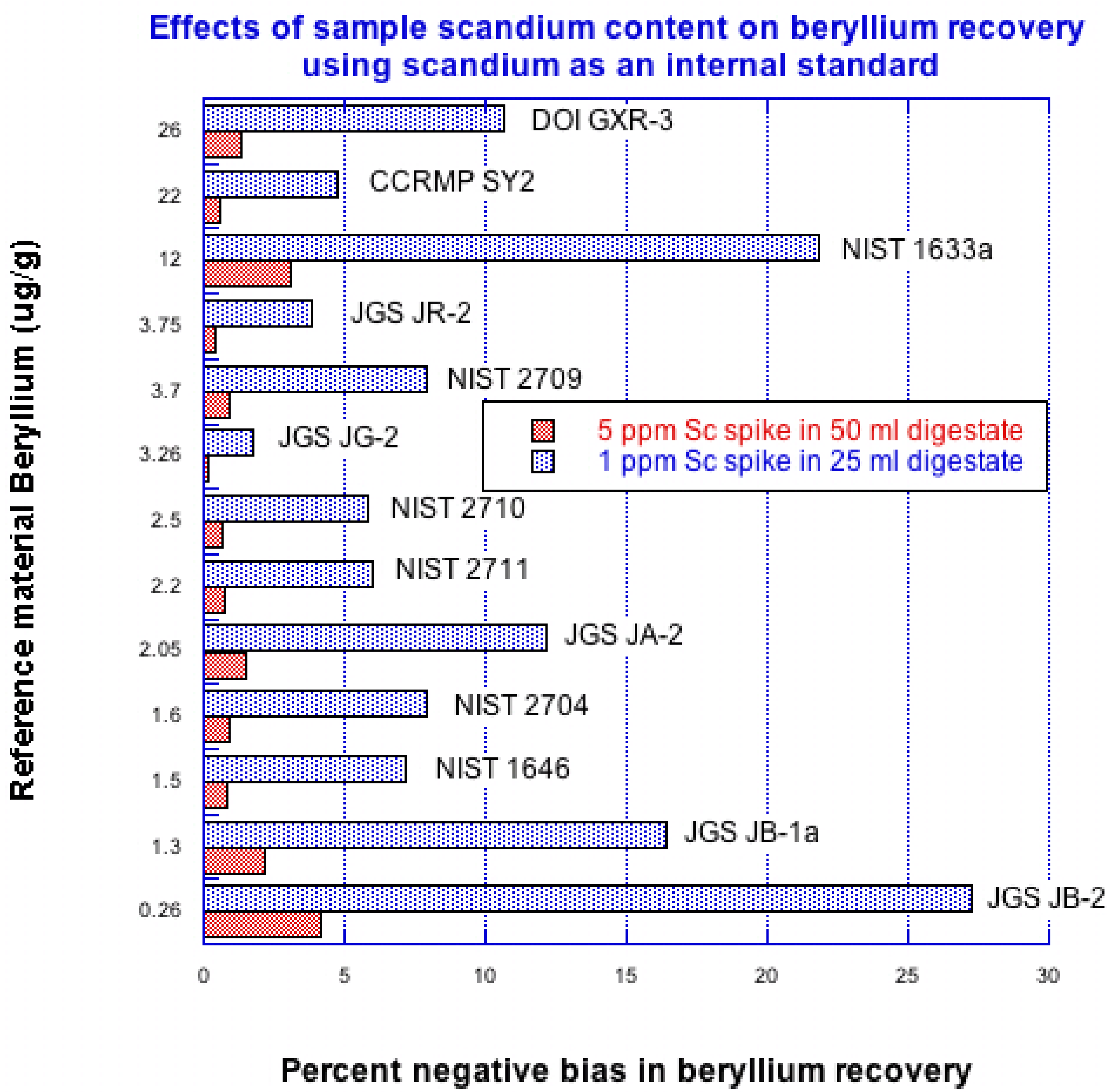
- **Lutetium (261.542 nm) at 1 ppm for samples high in scandium**

  requires absence of HF in digestate, or addition of boric acid to bind fluoride ions

Negative bias in beryllium measurement due to internal standard element in sample

	Beryllium is present	Beryllium is absent
Detected	**Correct decision**	**Incorrect Decision: False Positive (Type I error)**
Not detected	**Incorrect decision: False Negative (Type II error)**	**Correct decision**

NETL



Effects of sample scandium content on beryllium recovery using scandium as an internal standard
Reference material Beryllium (ug/g)
26
22
12
3.75
3.7
3.26
2.5
2.2
2.05
1.6
1.5
1.3
0.26
DOI GXR-3
CCRMP SY2
NIST 1633a
JGS JR-2
NIST 2709
JGS JG-2
NIST 2710
NIST 2711
JGS JA-2
NIST 2704
NIST 1646
JGS JB-1a
JGS JB-2
5 ppm Sc spike in 50 ml digestate
1 ppm Sc spike in 25 ml digestate
0
5
10
15
20
25
30
Percent negative bias in beryllium recovery

Minimizing negative beryllium values: the NETL-Albany approach

- Apply multivariate spectral deconvolution (MSF) to avoid negative bias found in Peak Area and IEC methods.
- Generally use four major interferences in model (Zr, V, Ti and Cr).
- Inspect residual plots for addition minor interferences and rerun samples as necessary.
- Maximize instrument response by use of high efficiency nebulizer/spray chamber system.
- Minimize internal standard biases.
- Use DDI water as the calibration blank to obtain a true zero calibration standard.
- Use larger wipe areas (512 cm2) to improve sampling precision.

Allows use of ProUCL statistical capabilities to evaluate beryllium wipe/bulk sample data

EPA ProUCL features:

- **Standard classical statistics**
- **Upper confidence tests (e.g. 95/95 UCL%)**
  - Students t
  - Normal
  - lognormal
  - Gamma
  - Non-parametric
- **Graphics (Histogram, Q-Q, box plots)**
- **Outlier tests (Dixon, Rosner)**

Source: http://www.epa.gov/esd/tsc/software.htm

Conclusions

- **Multivariate spectral deconvolution methods (e.g. MSF) are:**
  - Accurate for total beryllium analysis of wipe and bulk samples in the presence of metal alloy and alumino-silicates.
  - PerkinElmer method is faster while the NETL method is marginally more accurate.
- **Consider substituting optical fluorescence analysis using (ASTM D7458) to obtain comparable beryllium data quality, while reducing analysis complexity and analysis time.**

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